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The Vibration Spectra and Electric Moments of Azomethane, N−N′ Dimethylhydrazine and Acetaldazine

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The investigations reported here on azomethane, $CH_3 \cdot N=N \cdot CH_3$, N−N′ dimethylhydrazine, $(CH_3)HN \cdot NH(CH_3)$, and acetaldazine $(CH_3)HC=N-N=CH(CH_3)$ were carried out primarily to obtain information on the general form and some of the structural properties of these molecules, which are of a type whose chemical behavior with respect to thermal and photodecomposition is of considerable current interest. The properties examined have included the Raman spectra, with the state of polarization of the stronger lines, in the liquid state, and the electric moment in solution of the three compounds; the infrared absorption spectrum of azomethane vapor has also been investigated to the degree possible with the resolution ordinarily obtained from a rocksalt prism spectrometer.

THE electron diffraction pattern of azomethane, studied by H. Boersch,[1] indicates a C−N distance of 1.47±0.06A and a N−N distance of 1.24±0.05A, the former distance being the normal single bond C−N distance, and the other nearly the normal double bond N−N distance.[2]

The patterns did not permit an unambiguous differentiation between the *cis* and *trans* arrangements of the methyl groups in the molecule (or even a definite exclusion of a nonplanar form), but did eliminate the linear arrangement of carbon and nitrogen atoms, and, arguing from the absence of a permanent electric moment in azobenzene, Boersch concludes that the transplanar model is the best representation of azomethane. To anticipate our experimental results, the Raman and infrared spectra we have found exhibited by azomethane are in fact those of a molecule possessing a symmetry center, which, along with the zero moment the substance is found to have in heptane solution, and Boersch's elimination of the linear model, indicate conclusively a *trans* arrangement of the methyl groups in the azomethane molecule.

The structure of the hydrazines becomes particularly interesting in view of the conclusion of Penney and Sutherland[3] as to the strong asymmetry of hydrazine. Like that of hydrazine, the Raman spectrum of N−N′ dimethylhydrazine is that characteristic of an asymmetric molecule, and the electric moment in heptane solution is distinctly greater than zero. Assuming a skeleton for dimethylhydrazine similar to that proposed by Penney and Sutherland for hydrazine, one finds three possible isomers for the compound, of different theoretical electric moments, of which one is found to be in good agreement with the observed moment.

[1] H. Boersch, Monatsch. **65**, 311 (1935).
[2] L. Pauling and M. L. Huggins, Zeits. f. Krist. **87**, 205 (1934).
[3] W. G. Penney and G. B. B. M. Sutherland, Trans. Faraday Soc. **30**, 898 (1934). J. Chem. Phys. **2**, 492 (1934).

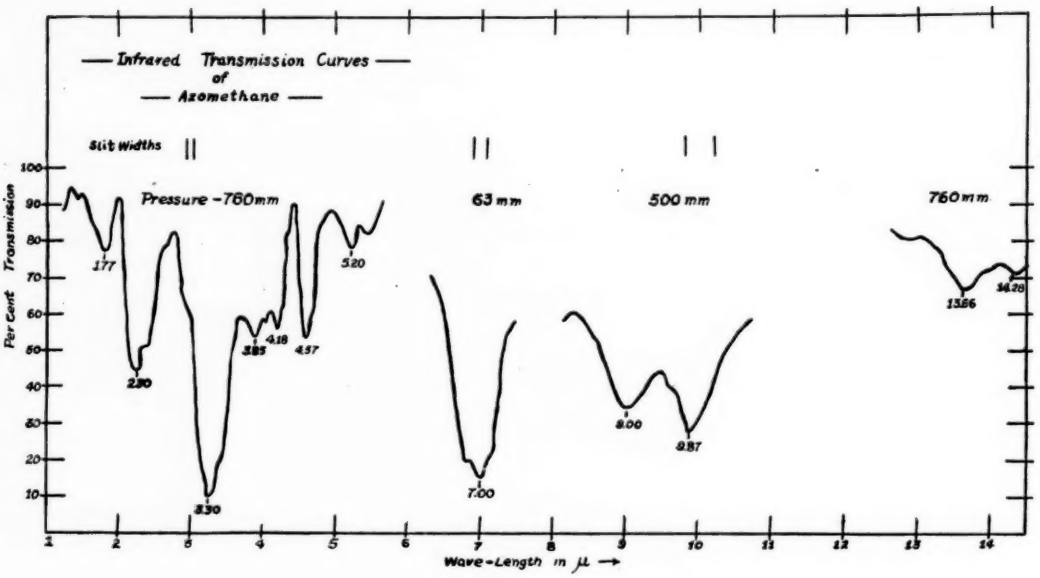


FIG. 1.

EXPERIMENTAL PROCEDURE

Dimethylhydrazine hydrochloride, required for the preparation of dimethylhydrazine and azomethane, was prepared by the method of Hatt.[4]

From this the base was liberated by the action of sodium hydroxide solution, in an apparatus connected to a vacuum line, due precautions (refluxing over barium oxide) being taken to remove water. The final distillation was directly into the Raman cell. The color, b.p. (80.5°), density (0.827), and refractive index (1.4201 for *D*) indicated high purity.

Azomethane was prepared by oxidation of dimethylhydrazine hydrochloride by Thiele's method,[5] purified by fractional distillation at −80°C through condensers cooled by dry ice into receivers in liquid air, and finally distilled as a colorless liquid into the Raman cell cooled by dry ice. Between exposures, azomethane, b.p. 1.5°C was allowed to evaporate into a large evacuated flask connected to the Raman cell to prevent the accumulation of pressures above atmospheric of this explosive compound.

Acetaldazine was prepared from acetaldehyde and hydrazine hydrate by the method of Curtius.[6]

[4] H. H. Hatt, *Organic Synthesis*, Vol. 16 (John Wiley and Sons, Inc., New York, 1936), p. 18.
[5] J. Thiele, Ber. 42, 2576 (1909).
[6] T. Curtius, J. Prak. Chem. 58, 325 (1898).

Raman spectrum

Filtered mercury radiation, 4358A and 4047A, was used to photograph the spectra; the dispersion was 90 cm^{-1} per mm at 4400A. Since azomethane was found to absorb in the near ultraviolet with the production of a crystalline solid, the scattering for wave-length 4358A was alone investigated in this case.

The small volume of the Raman cell (3 cc) made rather long exposures necessary, during which, in experiments on azomethane, the accumulation of frost on the cell or Dewar had to be prevented. A sheet metal box, into which the Raman cell fitted, was mounted rigidly in the Dewar, with the necessary passages for entry and exit of light sealed air-tight to the inner wall of the Dewar by moulding plaster, and provided with desiccant. A glass tube with window, mounted in the same way on the outer wall towards the spectrograph kept the passage of the scattered light clear, while a fan directed on the place of incidence of the exciting light on the outer wall prevented frosting here.

To measure the depolarization factors of the scattered lines, a Wollaston prism was placed in front of the camera lens and the densities of the double spectrum measured by a Moll microdensitometer, due regard being taken to ensure parallelism of the incident light by passing it

through vertical slots,[7] and to avoid spurious reflections. On the same plate intensity marks were made by photographing the spectrum of an incandescent bulb of accurately known variable intensity also resolved into perpendicular and parallel components by the Wollaston. A calibration curve showing the relation between light intensity and photographic density was made, and at the same time the correction to be applied owing to the greater loss by reflection at the surfaces of the optical parts of the spectrograph of the vertical component of the light was found. The degree of depolarization of the Raman lines of CCl_4 evaluated in this way agreed to within 0.03 with the values of Cabannes and Rousset.[8]

Infrared spectrum

The infrared absorption spectrum of azomethane was measured by use of a rocksalt prism instrument with a 60° prism of 5 cm base, mirrors at f : 6 and 36 cm focal length, a Moll linear thermopile and Leeds and Northrup H.S. low resistance galvanometer. A globar served as source. The absorption cell was 20 cm long, with rocksalt windows. The pressures of azomethane used are indicated in the curve (Fig. 1).

Dielectric constant measurements

The dielectric constants of solutions of the substances in *n*-heptane were measured by the heterodyne method at a frequency of 3.5×10^6 c.p.s. The oscillator was built by Dr. R. L. Garman of this department, and was essentially similar to that described by Stranathan,[9] in which the chief feature is the almost complete elimination, by adequate shielding and temperature control, of frequency drift. In view of the relatively high frequency used, special precautions were made to eliminate inductance errors introduced by the leads by exact mechanical as well as electrical substitution of the measuring cell for the standard condenser. The dielectric cell was calibrated against benzene, dielectric constant 2.279, and ether, dielectric constant 4.240, both at 25°C.

The cell, of the general design of Smyth and Morgan,[10] held 6 cc of solution. The method of filling the cell with azomethane solution of known composition should perhaps be described in a little detail. A weighed glass trap, provided with a side arm with stopcock, and with a capillary syphon reaching to the bottom, was attached, after the introduction of a weighed amount of heptane, by means of the side tube to the vacuum line used for the generation of azomethane. The trap was immersed in liquid air, with consequent freezing of the heptane, evacuated, and solid azomethane allowed to condense on the heptane, in which it dissolved when the temperature was allowed to rise. The weight of the solution was determined and the composition ascertained. To transfer the solution to the dielectric cell, the capillary syphon was connected to the cell by a ground joint and the solution carefully pushed over by means of dry air.

Densities were determined in a 1 cc pyknometer and refractive indices conveniently measured by squirting a few drops of solution from a medicine dropper through the drainage

TABLE I. *Vibration spectrum of azomethane.*

RAMAN (LIQUID) AT −60°C			INFRARED (GAS) AT 20°C	
$\Delta\tilde{\nu}$(cm^{-1})	I	ρ_n	$\lambda(\mu)$	$\tilde{\nu}$(cm^{-1})
548	1			
596	8	0.3		
			14.28	700
			13.66	730
922	4			
1023	1		9.87	1013
			9.00	1110
1182	3			
1376	5	*D**		
1442	9	.6	7.00	1430
1576	4			
			5.20	1923
			4.57	2190
			4.18	2392
			3.85	2597
2733	2			
2854	2			
2914	10	.25		
2985	8	*D*		
			3.30	3030
			2.30	4360
			1.77	5650

* *D* indicates a line too feeble to permit an accurate estimation of ρ_n but which was strongly depolarized.

[7] A. Langseth, J. U. Sørensen and J. R. Nielsen, J. Chem. Phys. **2**, 402 (1934).
[8] J. Cabannes and A. Rousset, Ann. de physique **19**, 229 (1933).
[9] J. D. Stranathan, Rev. Sci. Inst. **5**, 334 (1934).
[10] C. P. Smyth and S. O. Morgan, J. Am. Chem. Soc. **50**, 1547 (1923).

outlet between the prisms of an Abbe refractometer. No appreciable loss of solute by evaporation occurred in the time of a measurement. All measurements connected with electric moment estimations were made at 25°C.

The corresponding measurements on dimethyl hydrazine and acetaldazine were carried out in essentially the same way, with greater ease owing to their lower volatility than that of azomethane.

Results

Azomethane

Figure 1 shows the infrared absorption spectrum of azomethane, and the data on the infrared and Raman spectra are collected in Table I. The column headed I gives a rough estimate of relative intensities of Raman bands, and a crude estimate of the relative intensities of the absorption bands can be made from the pressures at which the different bands shown in Fig. 1 were measured.

ρ_n is the depolarization factor of the scattered radiation for unpolarized incident light =

$$\frac{\text{intensity of scattered light whose electric vector vibrates } \parallel \text{ to direction of incident beam}}{\text{intensity of scattered light whose electric vector vibrates } \perp \text{ to direction of incident beam.}}$$

Dielectric constant measurements

In Table II are summarized the measurements and the derived polarizations for azomethane dissolved in n-heptane at 25°C. c is the mole fraction of azomethane, d the density, ϵ the dielectric constant, n_D the refractive index for D, P_{12} the total molar polarization of the solution, P_1 the total polarization of azomethane in solution and P_1^0 the electronic polarization of azomethane in solution, calculated from refractive indices for D. Under each value of P_1^0 is a bracketed figure 5 percent less, which is taken to be the value of the electronic polarization for a static field. The measured values of the relevant constants for n-heptane required in the computation of P_1 and P_1^0 were, $\epsilon=1.920$, $d=0.6794$, $n_D=1.3867$, yielding P_2, the total molar polarization of heptane, equal to 34.50 cc.

TABLE II. *Dielectric constants and polarizations of azomethane in n-heptane at 25°C.*

c	d_4^{25}	ϵ	n_D	P_{12} cc	P_1 cc	P_1^0 cc
0.1477	0.6841	1.901	1.3819	31.707	15.572	16.249 (15.49)
0.0872	0.6821	1.909	1.3839	32.864	15.642	16.378 (15.63)
0.0619	0.6810	1.912	1.3849	33.358	16.010	16.769 (16.02)
					Mean 15.74	15.72

It is immediately clear that there is no excess in the total molar polarization of azomethane in these solutions over the electronic contribution, indicating the absence of a permanent electric moment in azomethane under these conditions.

N – N′ dimethylhydrazine and acetaldazine

Table III summarizes the Raman spectra of these compounds, and Table IV the dielectric measurements. In these cases the electronic polarization, P_1^0, has been calculated from the refractive indices and densities of the pure substances, a procedure justified by the well-known independence, to a first approximation, of this quantity on the state of aggregation of the substance. The relevant data are, for the hydrazine, $n_D=1.4194$, $d_4^{25}=0.8270$, and for acetaldazine, $n_D=1.4401$, $d_4^{25}=0.8311$. Incidentally, we have also found the dielectric constant of acetaldazine at 25° to be 4.435 ± 0.005. The total polarizations of the compounds in solution show no distinct trend with concentration, and we have considered it best to take the mean value in calculating the electric moment from the equation $\mu=0.0127((P_1-P_1^0)T)^{\frac{1}{2}}$ Debye units. Permanent moments of 1.35 ± 0.15 and 1.16 ± 0.10 D are found for dimethyl hydrazine and acetaldazine respectively in heptane at 25°C.

Discussion of Results

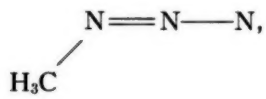
Azomethane

We recall again Boersch's elimination of a linear structure for this molecule by electron diffraction experiments, a conclusion consistent with the structure proposed by Brockway and Pauling[11] for methylazide,

[11] L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. **19**, 860 (1933).

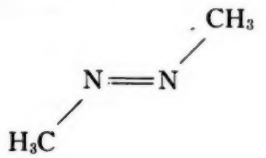
TABLE III. *Raman spectra of N−N′ dimethylhydrazine and acetaldazine at 20° C.*

N−N′ DIMETHYLHYDRAZINE			ACETALDAZINE		
$\Delta\nu(cm^{-1})$	I	ρ_n	$\Delta\nu(cm^{-1})$	I	ρ_n
473	2	D	374	0	
1010	2		499	5	0.3
1118	2		907	4	D
1201	2		1029	3	D
1301	2		1151	4	D
1465	5		1345	5	D
2790	6	0.25	1389	4	D
2838	4	D	1443	5	.8
2867	4	D	1530	0	
2940	10	.25	1569	2	
2973	9	D	1627	10	.6
3099	3		2866	2	
3226	10	.3	2925	8	.3
3319	6	D	2959	2	
3390	2				



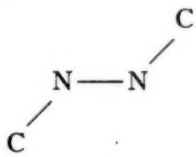
with a C−N−N angle of 135°±15°. On the assumption of lack of free rotation in the nitrogen-nitrogen linkage, we have then the alternatives of distinct *cis* or *trans* forms of azomethane; and the absence of a permanent moment, within our limits of detection, shows immediately and unambiguously that in inert solvents at 25°, the substance is nearly all in the *trans* form. The analogy between azomethane and *p−p′* dibromazobenzene, from whose zero moment Boersch had already concluded that the *trans* form was the most likely structure for azomethane, is therefore a valid one.

The spectral results are also in accord with a *trans* configuration. The structure



has a center of symmetry, the corresponding *cis* form has not; the former form will have two sets of fundamental frequencies, one of which will be active in Raman scattering only, the other in infrared absorption only; for the *cis* form the excitation of certain modes of vibration by both mechanisms will be possible. In the Raman spectrum of liquid azomethane we have found 12 relatively strong frequencies, half of the total $3n-6=24$ vibrations the molecule may possess; the infrared absorption, exclusive of frequencies greater than 3030 cm^{-1}, as we have observed it in the gas, consists of 10 bands. Not all of these are likely to be fundamentals, e.g., the bands at 2392 cm^{-1} and 2597 cm^{-1}; also, the band whose maximum is at 3030 cm^{-1} and possibly some of the others, are almost certainly unresolved complexes of fundamentals, so we do not know how many fundamentals are active in infrared absorption; but the significant point is that with the pronounced exception of the strong Raman frequency 1442 cm^{-1} and the strong infrared frequency 1430 cm^{-1} there is no coincidence of Raman and absorption frequencies.

The skeleton



has the symmetry C_{2h}, which will have three modes of vibration symmetrical to the symmetry center, active in scattering, and three antisymmetrical, active in absorption of light.[12] In fact, apart from the frequencies of the hydrogen atoms in the methyl radical, the Raman frequencies of azomethane group themselves into three sets,

TABLE IV. *Polarizations of N−N′ dimethylhydrazine and acetaldazine in heptane at 25°C.*

N−N′ dimethyl hydrazine					
c	d_4^{25}	ϵ	P_{12} cc	P_1 cc	P_1^0 cc
0.0942	0.6872	2.046	36.245	54.732	17.640
.0523	.6841	1.988	35.495	56.700	"
.0332	.6824	1.951	34.846	50.020	"
.0177	.6810	1.931	34.578	52.350	"
				Mean 55.21	
Acetaldazine					
0.3024	0.7192	2.865	41.422	57.80	26.66
.0953	.6918	2.031	36.449	56.47	"
.0855	.6904	2.026	36.437	56.08	"
.0221	.6822	1.932	34.662	49.57	"
				Mean 54.43	

[12] G. Placzek, *Handbuch der Radiologie*, Vol. VI. 2. p. 293 (Akad. Verlags gesellschaft, Leipzig, 1934).

around the strong frequencies 1442 cm^{-1}, 922 cm^{-1}, and 596 cm^{-1}. These we ascribe to totally symmetrical vibrations of the azomethane molecule; and one other member in each group will be due to a vibration, symmetrical to the symmetry center, in which the phase of one of the hydrogen atoms in each methyl group is opposite to that of the other two. The approximate vibration forms of the carbon-nitrogen skeleton with their proposed frequencies are shown in Fig. 2, in which the motions of the nuclei in ν_4 and ν_6 take place perpendicularly to the molecular plane.

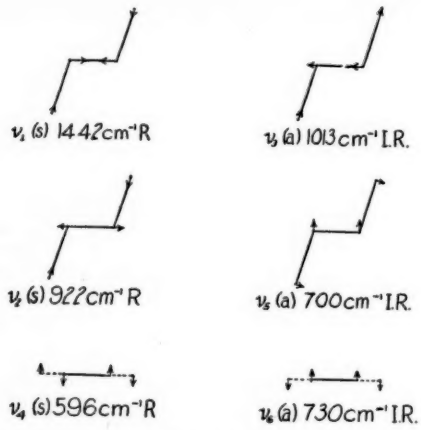


FIG. 2.

In the vibrational mode ν_1 the two nitrogen nuclei are those which have the greatest amplitude of motion, and in the language of "bond frequencies," we might call this the N=N bond frequency in azomethane and similarly ν_2 the C−N frequency. The value 1442 cm^{-1} for the N=N frequency in azomethane seems at first sight rather low, in the light of the well-known values of 1620 to 1650 cm^{-1} for the C=C frequency in ethylenic compounds, and 1710 to 1760 cm^{-1} for the C=O frequency in aldehydes and ketones. The diatomic N_2 molecule, however, has two excited states, immediately above the lowest state, each with 2 net pairs of bonding electrons, which would be described in the inadequate language of the chemical theory of valence as double bonded.[13]

The lower state, $^3\Sigma_u^+$, with the electronic configuration $\sigma_g^2\sigma_u^2\pi_u{}^3\sigma_g^2\pi_g$, has an equilibrium internuclear distance of 1.290A and a frequency of 1460 cm^{-1} (cf. the Pauling-Huggins N=N distance 1.26A and the other, $^3\Pi_g$, $\sigma_g^2\sigma_u^2\pi_u{}^4\sigma_g\sigma_u$, an internuclear distance of 1.207A and a frequency of 1733 cm^{-1}. The electronic states immediately above the normal state of the isoelectronic molecule CO are a state K of unknown characteristics and a $^3\Pi$, $\sigma^2\sigma^2\pi^4\sigma\pi$ of internuclear distance 1.205A and frequency 1739 cm^{-1}. The Pauling-Huggins distance for C=O is 1.28A. It seems probable that the state of CO in the carbonyl radical of the aldehydes and ketones can be regarded as derived from the $^3\Pi$ state of CO, and it is evident that the corresponding N=N state in a complex molecule would have a frequency of about 1700 cm^{-1} and an internuclear distance of somewhat under 1.20A. The observed frequency of 1440 cm^{-1} and internuclear distance of 1.24A of the N=N bond in azomethane seem reasonably to be derived largely from the $^3\Sigma_u^+$ state of the diatomic molecule. Our conclusion therefore is that the Raman frequency 1442 cm^{-1} in azomethane does represent the N=N vibration frequency, and that this bond is not analogous to the C=O bond, but is one with essentially weaker binding.

The origin of the strong infrared absorption at 1430 cm^{-1} has still to be discussed. The evidence for the structure proposed for azomethane is very strong, and granting its correctness, according to the selection rules for molecules with symmetry centers, the infrared absorption in question cannot be associated with the N=N vibration. The near coincidence between the absorption and Raman frequency must be accidental. Its obvious origin is in an antisymmetric bending vibration of the H atoms in the methyl groups, which is well known to have a value about 1430 cm^{-1} and which is a prominent feature of the absorption spectrum of most compounds containing methyl groups; the fairly strong Raman frequency 1376 cm^{-1} may be the corresponding symmetrical mode.

N·N′ dimethylhydrazine

In the light of Penney and Sutherland's proof of the strong asymmetry of the hydrazine molecule, it is not surprising that dimethylhydrazine likewise shows the characteristics of a strongly asymmetric molecule. In the Raman spectrum

[13] H. Sponer, *Molekulspektren-Tabellen* (Julius Springer, Berlin, 1935), pp. 11 and 32.

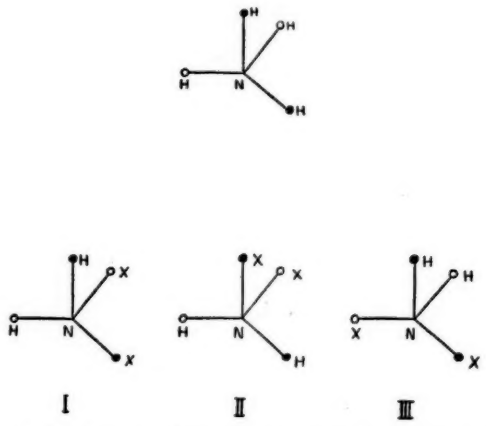


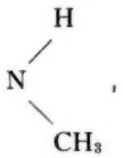
FIG. 3. "End-on" views of hydrazine and the structurally possible N−N disubstituted hydrazines.

there are no strong lines except those corresponding to the C−H and N−H vibrations around 2900 cm^{-1} and 3300 cm^{-1}, respectively, and in particular there is no strong line of about 1000 cm^{-1} in the position to be expected if the two halves of the molecule could exercise a symmetrical vibration with respect to one another. The relatively high value of the electric moment, 1.35 *D* is practically certain evidence of asymmetry.

We shall assume that the asymmetry in dimethylhydrazine is essentially like that in hydrazine. In the latter molecule, Penney and Sutherland show that, as a result chiefly of the hindrance to free rotation about the N−N bond caused by the interaction of the axially unsymmetrical wave functions of the nitrogen atoms, the most stable arrangement is that in which the bonds radiate from each nitrogen atom at about the tetrahedral angle of 110° and in which the one NH_2 group is twisted with respect to the other in such a way that the projections of the NH bonds on one nitrogen atom on a plane perpendicular to the N−N axis have been rotated through 90° with respect to those on the other nitrogen atom.

Three possible structures are now open for a disubstituted hydrazine with the substituents on different nitrogen atoms which are represented in Fig. 3 as I, II and III.

Assuming the valence angles in dimethylhydrazine the same as those given by Penney and Sutherland for hydrazine, and also assuming that the resultant moment of a molecule is additively compounded of the various "bond moments" present[14] we can compute the moment of the three structures and compare it with experiment. The observed moment of ammonia leads to the value of 1.30 *D* for the NH bond moment. Assuming now that in the amines the bonds radiate from the nitrogen atom at the tetrahedral angle, as in ammonia, and that in these compounds the negative end of the N−C moment is towards the nitrogen atom, we find from the observed moments of methylamine and trimethylamine, 1.23 and 0.6 *D*, respectively,[15] that the N−C bond moment is 0.61 *D*, and that the moment of the group



with the same assumption as to valence angles, is 1.28 *D* at an angle of 28° to the direction of the NH bond in the HNC plane. The N−N link in dimethylhydrazine, assumed to make angles of 110° with the NH and NC bonds, is found to make the angle 122° with the NH · CH_3 moments. To calculate the moment of the different structural modifications of dimethylhydrazine, one compounds the 2 moments of magnitude of 1.22 *D*, each at 122° to the N−N bond, and oriented with respect to each other in the different ways required by the three models. In this way structures I, II, and III are found to have moments of 1.47, 0.54 and 2.00 *D*, respectively, to be compared with the observed value of 1.35 ±0.15. Models II and III are definitely excluded as preponderant structures in dimethylhydrazine at room temperature; model I has a moment, which in view of the experimental uncertainty and the approximate nature of the assumptions on valence angles and additivity of bond moments made in the calculations, can be regarded as agreeing with the experimental value. It would be regarding the calculations too seriously to conclude that the somewhat lower experimental value of the moment than that calculated for structure I indicated the presence in dimethylhydrazine of a little of structure II; but what

[14] A. Eucken and L. Meyer, Physik. Zeits. **30**, 400 (1929).
[15] Trans. Faraday Soc. **30**, Appendix to general discussion on dipole moments, pp. lix, lx (1934).

seems certain is that dimethylhydrazine in heptane solution at 25°C is predominately of structure I.

Little can be added at present concerning the Raman spectrum of dimethylhydrazine to the general description already given. Two lines of 1010 cm^{-1} and 1118 cm^{-1} seem to be comparable with the pair at 904 cm^{-1} and 1117 cm^{-1} of hydrazine in aqueous solution,[16] of which one or other, or both, are due essentially to the N−N vibration, while the line at 473 cm^{-1} is probably due to the corresponding bending vibration. With respect to acetaldazine we wish at present only to emphasize the asymmetry in the structure indicated by the moment of 1.16 *D* and the identification of the strongest line in the Raman spectrum, corresponding to a frequency of 1627 cm^{-1} as the C : N vibration.

[16] K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (Julius Springer, Berlin, 1931), p. 312.

We desire to acknowledge the assistance extended by Dr. R. L. Garman in our measurements of the dielectric constants.

SUMMARY

The Raman spectra and electric moments of azomethane, N−N′ dimethylhydrazine and acetaldazine, and the infrared absorption of azomethane from 1–15μ are reported. The results indicate a *trans* configuration for azomethane, and an unsymmetrical structure for dimethylhydrazine, derived from Penney and Sutherland's structure for hydrazine. Some of the data are; electric moments, azomethane, O, N−N′ dimethylhydrazine, 1.35 *D*, acetaldazine, 1.10 *D*; N=N vibration frequency in azomethane 1442 cm^{-1}, C=N vibration frequency in acetaldazine, 1627 cm^{-1}, dielectric constant of acetaldazine at 25°, 4.435.

JANUARY, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6

Raman Spectra of Benzene and Isotope Effect

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A faint line accompanying the strong line in the region of 990 cm^{-1} is observed in the Raman spectra of benzene, chlorobenzene, bromobenzene, toluene and cyclohexane. The relative intensities of the weak 984 cm^{-1} line and the strong 992 cm^{-1} line of benzene are measured to be in the ratio 6 : 100. This together with an approximate theoretical estimate support the suggestion that the weak line is due to molecules in which one of the carbon atoms is an isotope of mass 13. The exceedingly low intensity of the corresponding faint line in cyclohexane seems to point to a nonplanar structure. Similar study on the 944 cm^{-1} line in C_6D_6 is suggested.

INTRODUCTION

THE Raman and the infrared spectra of benzene have been the subject of many investigations and the normal vibrations of the benzene molecule are well known.[1] Of the many Raman lines, the strong and polarized lines at 992 cm^{-1} and 3060 cm^{-1} are known to be the frequencies of the symmetrical pulsating motions of the carbon and the hydrogen rings.[2] The line at 992 cm^{-1} is accompanied by a very faint line at 984 cm^{-1}. It has been suggested by Gerlach[3] that this faint line may be due to a molecule in which one of the carbon atoms is replaced by a heavy isotope of mass 13. Attempt to settle this question by means of polarization measurement of the weak line by Grassmann and Weiler[4] has not been conclusive because of the difficulty in obtaining exact values for the degree of depolarization of an extremely weak line in close proximity with a very strong one.

[1] K. W. F. Kohlrausch, Physik. Zeits. **37**, 58 (1936).
[2] J. Weiler, Zeits. f. Physik **72**, 206 (1931).
[3] W. Gerlach, Münch. Ber. **39**, Nr. 1 (1932).
[4] P. Grassmann and J. Weiler, Zeits. f. Physik **86**, 329 (1933).

In this study, we attempt to verify the suggestion of Gerlach by (i) measuring the relative intensities of the 992 and 984 cm^{-1} lines, (ii) studying the corresponding lines in other derivatives of benzene, and (iii) making an approximate theoretical estimate of the isotope shift due to the replacement of one of the carbon atoms in the benzene ring by an isotope of mass 13.

Experimental

The Raman spectra were studied with the conventional set-up and a three-prism Steinheil glass spectrograph giving a dispersion of about 12A per mm at the position of the 992 cm^{-1} line of C_6H_6 when excited by the 4358A line of mercury. For intensity measurements, intensity marks were put on the plate by means of a step diaphragm and relative intensities determined according to the method of Thomson and Duffendack.[5] Exposures for the 992, 984 cm^{-1} lines varied from four to ten hours while the exposures for intensity marks were five minutes. Polarization measurements were made by means of a Hanle combination crystals as described elsewhere.[6]

Because of the closeness of the 992 and 984 cm^{-1} lines, they were also examined with a telesystem attached to the Steinheil spectrograph. The dispersion attained was about 3A per mm. The two lines were then clearly separated; but with the consequent decrease in intensity, exposures had to be prolonged to about 100 hours. With the polarization crystals, exposures of even 300 hours failed to register the depolarized component of the weak 984 cm^{-1} line although the polarized component was detectable. Because of the excessively long exposure and the difficulty in putting on intensity marks with the telesystem which brought only a very narrow spectral region into sharp focus, these plates were not used in the actual intensity measurements.

In Fig. 1 is reproduced a spectrogram of the Raman lines 992–984 cm^{-1} of benzene excited by the 4358A Hg line. A typical microphotometer tracing of the two lines is given in Fig. 2. In determining their relative intensities, an intensity curve for the contour of the two lines was plotted by means of the blackening-log intensity curve. Account is taken of the partial overlapping of the two lines and the presence of the continuous background in the spectrum. The relative intensities of the two lines as measured on four separate plates were 100 : 5, 100 : 6, 100 : 6, and 100 : 7. When allowance is made for the uncertainty introduced by the partial overlapping of a strong and a weak line, these values are as close as one can expect, and the average value of 100 : 6 cannot be very much in error.

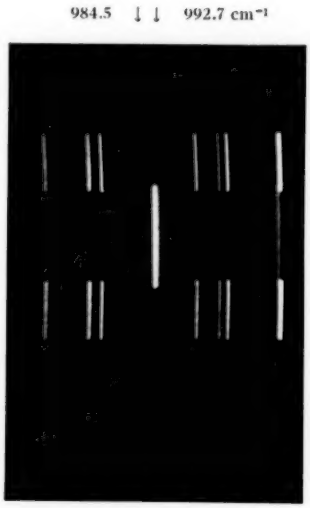

Fig. 1. Raman lines 992, 984 cm^{-1} of benzene.

The relative abundance of the carbon isotopes of mass 12 and 13 has been determined by a number of authors using spectroscopic, mass-

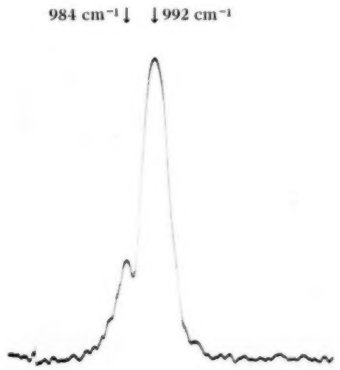

Fig. 2. Microphotometer curve of 992, 984 cm^{-1} Raman lines of benzene.

[5] K. B. Thomson and O. S. Duffendack, J. Opt. Soc. Am. **23**, 101 (1933).
[6] Shen, Yao and Wu, Phys. Rev. **51**, 235 (1937).

spectrograph and chemical methods.[7] The value arrived at by all is about 100 : 1. Considering the presence of six identical carbon atoms in the symmetrical benzene molecule, one would expect the relative abundance of the $C_6{}^{12}H_6$ and $C_5{}^{12}C_1{}^{13}H_6$ molecules to be in the ratio 100 : 6. The exact agreement between this value and the relative intensities of the 992 and 984 cm^{-1} lines of benzene seems to support strongly the suggestion that the weak line 984 cm^{-1} is due to an isotope effect of carbon in the benzene molecule.

It is hence desirable to examine the lines corresponding to the 992 cm^{-1} line of benzene in the Raman spectra of other derivatives. The results of the study on chlorobenzene, bromobenzene and toluene are tabulated in Table I.

TABLE I.

	ν_1(strong)	ν_1(weak)	$\Delta\nu$
Benzene	992 cm^{-1}	984 cm^{-1}	8 cm^{-1}
Chlorobenzene	1001	990	11
Bromobenzene	1000	993	7
Toluene	1004	993	11

Due to the weakness of one and the diffuseness of the two lines, these frequencies are probably accurate only to 1 cm^{-1}, and the difference between the two may be in error by 2 cm^{-1}. The significant point is that in each of these molecules, a much weaker line of lower frequency shift by about 8 cm^{-1} accompanies the strong line in the region of 990 cm^{-1}. Exact intensity measurement of the two lines in the derivatives could not be made on account of the rather strong background. But a rough estimate of their relative intensities and the order of magnitude of their frequency difference make it probable that the weak line has its origin in a molecule having one carbon isotope of mass 13.

An attempt to measure the degree of depolarization ρ of the 984 cm^{-1} line of benzene was made. Exposure of even 100 hours (without the use of telesystem) still failed to bring out the depolarized component while the polarized component was easily measurable. Thus although no numerical value has been obtained, we can with certainty place an upper limit for ρ at 0.40 and can safely say that it is probably lower. Hence it appears that the polarization characters of the 992 and the 984 cm^{-1} lines are the same.

Another molecule of considerable interest is cyclohexane C_6H_{12}. If the form of the molecule is one in which the six carbon atoms do not lie in one plane, then there will still be a faint line accompanying the 800 cm^{-1} line which polarization measurement[8] and theoretical calculation show to correspond to the symmetric vibrations of the carbon and hydrogen atoms, but the relative intensities would be lower than in the case of benzene, because of the lower symmetry. If the molecule is a plane, symmetric one, then one would expect the 800 cm^{-1} line to be accompanied by a weak line whose intensity is 6/100 of the 800 cm^{-1} line. Prolonged exposures of the Raman spectrum of cyclohexane show that while the microphotometer curve revealed a faint kick about 6 cm^{-1} to the low frequency displacement side of the 800 cm^{-1} line, their relative intensities are definitely much lower than the ratio 6:100 expected for a plane, symmetric model. The exceedingly low intensity of the weak line precludes any intensity or polarization measurement. All one can say is that from isotope shift consideration it seems that the plane, symmetric model is incompatible with the observed intensity ratio.

THEORETICAL CALCULATION

To examine further the possibility that the weak line 984 cm^{-1} in benzene may be due to the replacement of one of the six carbon atoms by an isotope of mass 13, we may make an approximate estimate of such an isotope shift by the "perturbation theory" method of Wilson.[9] The treatment of the normal vibrations of benzene by Wilson[10] shows that the frequencies of the two totally symmetric pulsating motions of the carbon and the hydrogen rings separate from the other frequencies in the determinantal equation. Following Wilson, let us denote the radial displacements of the carbon atoms, mass M, and the hydrogen atoms, mass m, by R and r,

[7] Baxter and Hale, J. Am. Chem. Soc. **59**, 506 (1937).

[8] K. W. F. Kohlrausch and W. Stockmair, Zeits. f. physik Chemie **B31**, 382 (1936).

[9] E. B. Wilson, Phys. Rev. **45**, 427 (1934).

[10] E. B. Wilson, Phys. Rev. **45**, 706 (1934); **46**, 146 (1934).

respectively. On introducing the generalized coordinates $Q_1=(6M)^{\frac{1}{2}}R$, $Q_2=(6m)^{\frac{1}{2}}r$, the kinetic energy becomes

$$T=6/2[M\dot{R}^2+m\dot{r}^2]=1/2[\dot{Q}_1^2+\dot{Q}_2^2]$$

and the potential energy

$$V=6/2[KR^2+q(R-r)^2]$$
$$=1/2[(K+q)Q_1^2/M-2qQ_1Q_2/(Mm)^{\frac{1}{2}}+qQ_2^2/m]$$

where K is the force constant between two neighboring carbon atoms and q the force constant between C−H atoms. Let the normal coordinates X, Y for the vibrations $\nu_1=992$, $\nu_2=3060$ cm^{-1} be defined through the transformation equations

$$\begin{aligned} Q_1&=a_{11}X+a_{12}Y,\\ Q_2&=a_{21}X+a_{22}Y. \end{aligned} \tag{1}$$

The determinantal equation is

$$\lambda^2-[(K+q)/M+q/m]\lambda+qK/Mm=0 \tag{2}$$

where $\nu=(\lambda)^{\frac{1}{2}}/2\pi$. Solution of this equation with $\nu_1=992$, $\nu_2=3060$ cm^{-1} gives $K=7.50\times10^5$, $q=5.05\times10^5$ dynes/cm. The transformation coefficients are readily obtained.

$$\begin{aligned} a_{11}&=k_1(m\lambda_1-q)/m, \quad a_{21}=k_2(m\lambda_2-q)/m,\\ a_{12}&=-k_1q/(Mm)^{\frac{1}{2}}, \quad a_{22}=-k_2q/(Mm)^{\frac{1}{2}}, \end{aligned} \tag{3}$$

where
$$\begin{aligned} k_1&=[(\lambda_1-q/m)^2+q^2/mM]^{-\frac{1}{2}},\\ k_2&=[(\lambda_2-q/m)^2+q^2/mM]^{-\frac{1}{2}}. \end{aligned}$$

When one of the particles of mass M is replaced by one of mass $M+\Delta M$, the change in the potential energy is

$$\Delta V=1/12[-(K+q)\Delta MQ_1^2/M^2 +q\Delta MQ_1Q_2/M(Mm)^{\frac{1}{2}}]. \tag{4}$$

The isotope shifts $\Delta\nu=\Delta\lambda/8\pi^2\nu$ are given according to the perturbation method by

$$\begin{aligned} \Delta\lambda_1&=1/6[-(K+q)\Delta Ma_{11}^2/M^2 +q\Delta Ma_{11}a_{12}/M(Mm)^{\frac{1}{2}}],\\ \Delta\lambda_2&=1/6[-(K+q)\Delta Ma_{12}^2/M^2 +q\Delta Ma_{12}a_{22}/M(Mm)^{\frac{1}{2}}]. \end{aligned} \tag{5}$$

Substitution of $\Delta M=1$ and the known values of the various quantities in these two expressions gives $\Delta\nu_1\backsimeq-6.3$ cm^{-1} for the 992 cm^{-1} line, and $\nu_2\backsimeq-1.2$ cm^{-1} for the 3060 cm^{-1} line.[11] This shows that the difference between the 992 and 984 cm^{-1} lines is just of the correct magnitude of the isotope shift. The calculated shift of 1.2 cm^{-1} for the 3060 line also explains why no weak line is observed accompanying it, for one strong and one weak line so close together would simply appear as a single line in the Raman spectrum.

Entirely similar calculations on hexadeuterobenzene C_6D_6 give for the 944 cm^{-1} line a shift $\Delta\nu\sim-5$ cm^{-1} and for the 2292 cm^{-1} line a shift $\Delta\nu\sim-1$ cm^{-1}. However, a weak line accompanying the 944 cm^{-1} line has not been reported in the work of Wood[12] and Angus and his collaborators.[13] Also on the assumption of a plane symmetrical model, similar calculations give for cyclopentane C_5H_{10} an isotope shift of about 6 cm^{-1} for the strong and polarized line 886 cm^{-1}. It would be interesting to reexamine these lines under greater dispersion; for their presence would lend further support to the isotope theory for the 884 cm^{-1} line of benzene.

We are grateful to Dr. Y. T. Yao, director of this laboratory, for his constant inspiration, to Dr. C. L. Tseng, of the chemistry department, for the use of the chemicals, to Dr. Ny Tsi-Zé, of the National Academy of Peiping, for the use of the microphotometer. Our best thanks are due to Professor W. F. Colby, of the University of Michigan, who so kindly supplies some of the references to which we have at present no access on account of the conditions prevailing in Peiping.

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[11] From Eqs. (1) and (3), one can readily obtain the relative displacements of the carbon and the hydrogen atoms for the two normal vibrations; namely for $\nu_1=992$, $R/r\backsimeq0.9$, and for $\nu_2=3060$, $R/r\backsimeq-0.09$. Thus roughly speaking in the vibration ν_1, the carbon and the hydrogen rings contract and expand in phase with each other, while in the vibration ν_2, the two rings vibrate against each other, about 9/10 of the relative displacement being traversed by the hydrogen atoms. Simple calculations from Eq. (2) show that while ν_2 depends strongly on the force constant q, ν_1 depends strongly on K, the force constant for two neighboring carbon atoms.

[12] R. W. Wood, J. Chem. Phys. **3**, 444 (1935).

[13] Angus *et al.*, Nature **135**, 1033 (1935).

The Infrared Absorption of the OH Group of Phenol

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The fundamental vibrational band of the OH group of phenol appearing in the region of 3μ has been studied for solutions of different concentrations of phenol in benzene, bromobenzene, nitrobenzene, dioxane, and ethyl acetate. The band appears at the same position, 2.96μ, for the concentrated solutions in all the solvents. In dilute solution in benzene and bromobenzene it appears at 2.79μ. The band at 2.79μ is attributed to the OH of single molecules, while that appearing at 2.96μ in the more concentrated solutions is thought to be due to associated OH. In dilute solutions in the oxygenated solvents the band appears at wave-lengths longer than 2.79μ and is more intense than for the corresponding solution in benzene or bromobenzene. These results are regarded as evidence that the oxygenated solvents form weak additive compounds with the phenol by sharing the proton of the OH group.

IT has been suggested by other writers[1] that phenol in concentrated solutions in solvents such as benzene is probably associated through the formation of hydrogen bonds. It is thought that the phenols as well as the alcohols[1] and water form associated chains:

$$\begin{array}{cccc} R & R & R & \\ | & | & | & \\ H-O-H-O-H-O, & \text{etc.}, & & \end{array}$$

the oxygen of the hydroxyl group acting as donor and the hydrogen of this group acting as acceptor. Sidgwick suggests that this chain is not likely to contain more than three or four molecules. In extremely dilute solutions molecular weight measurements indicate that the chains are broken and that single molecules predominate. This view has been amply confirmed by infrared measurements for carbon tetrachloride solutions of the alcohols.[2] In these experiments the band which was attributed to the OH group of single molecules appeared at a shorter wave-length by about 0.25μ than that which was attributed to the associated OH group. Also, the absorption coefficient of the fundamental was less for the single molecules than for the associated ones. Fox and Martin[2] have reported similar evidence for the association of phenol in carbon tetrachloride solution. Spectroscopic data[3] has been reported favoring the association of water, with a difference of about 0.3μ in the position of the associated from that of the monomolecular band. In oxygenated or other solvents which contain a donor and can unite with the solute through the formation of hydrogen bonds, observations[4] show that a shift of the OH band of alcohol and of water occurs at rather high concentrations, although in dilute solution in these solvents the band appears at wave-lengths longer by about 0.10μ than the monomolecular band in dilute solution in carbon tetrachloride. Furthermore the band is more intense when the solvent contains a donor. These results have been advanced as evidence that the solute forms weak hydrogen bonds with solvents of this type.

Infrared evidence has been reported for the existence of intramolecular hydrogen bonds in some of the substituted phenols.[5] Certain *ortho* substituted atoms or groups, particularly C=O, affect appreciably the absorption of the phenolic OH: for example, the absorption curve of o-chloro-phenol shows two distinct peaks in the region 6500 cm^{-1} to 7200 cm^{-1}, one near that of

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[1] E. N. Lassettre, Chem. Rev. **20**, 259 (1937); N. V. Sidgwick, *The Electronic Theory of Valency* (Oxford University Press, 1929), pp. 134, 149.

[2] J. Errera and P. Mollet, Comptes rendus **204**, 259 (1937); J. J. Fox and A. E. Martin, Nature **139**, 507 (1937); E. L. Kinsey and J. W. Ellis, J. Chem. Phys. **5**, 399 (1937); A. M. Buswell, V. Deitz, and W. H. Rodebush, J. Chem. Phys. **5**, 501 (1937).

[3] E. L. Kinsey and J. W. Ellis, Phys. Rev. **51**, 1074 (1937); G. B. Bosschieter and J. Errera, J. de phys. et rad. **8**, 229 (1937).

[4] W. Gordy, Phys. Rev. **51**, 564 (1937); J. Chem. Phys. **4**, 769 (1936); J. Chem. Phys. **5**, 202 (1937); D. Williams and W. Gordy, J. Am. Chem. Soc. **59**, 817 (1937).

[5] O. R. Wulf, U. Liddel, and S. B. Hendricks, J. Am. Chem. Soc. **58**, 2287 (1936).

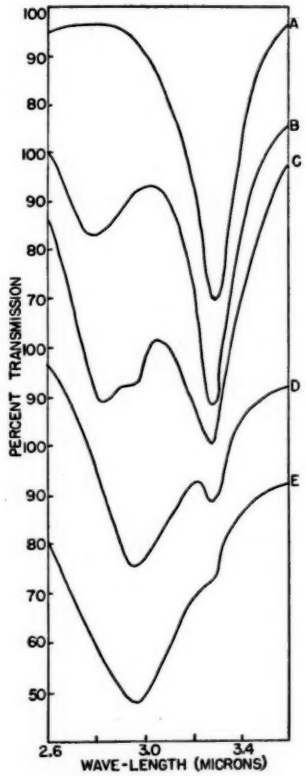

Fig. 1. Percentage transmission of phenol in benzene: *A*, pure benzene, cell thickness 0.007 cm; *B*, phenol 0.23 mole/lit., cell thickness 0.007 cm; *C*, phenol 0.95 mole/lit., cell thickness 0.003 cm; *D*, phenol 5 mole/lit., cell thickness 0.001 cm; *E*, phenol 8 mole/lit., cell thickness 0.001 cm.

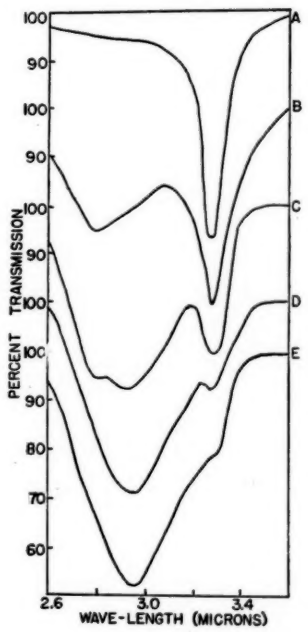

Fig. 2. Percentage transmission of phenol in bromobenzene: *A*, pure bromobenzene, cell thickness 0.007 cm; *B*, phenol 0.34 mole/lit., cell thickness 0.007 cm; *C*, phenol 1.4 mole/lit., cell thickness 0.003 cm; *D*, phenol 6 mole/lit., cell thickness 0.001 cm; *E*, phenol 9 mole/lit., cell thickness 0.001 cm.

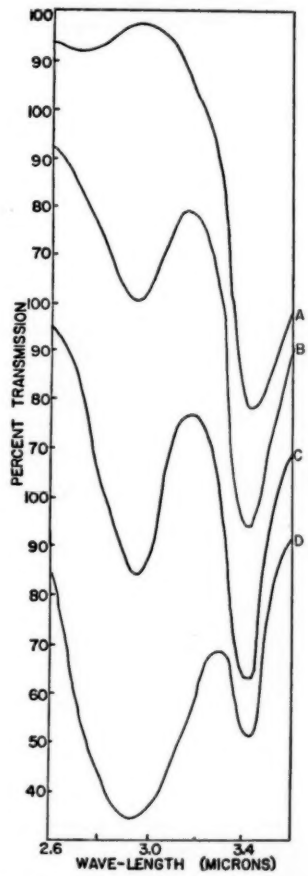

FIG. 3. Percentage transmission of phenol in dioxane: *A*, pure dioxane, cell thickness 0.007 cm; *B*, phenol 0.23 mole/lit., cell thickness 0.007 cm; *C*, phenol 0.95 mole/lit., cell thickness 0.003 cm; *D*, phenol 8 mole/lit., cell thickness 0.001 cm.

the single peak which occurs in the curve for phenol itself and one at slightly longer wavelengths. In some cases of *ortho* substitution the harmonic of the phenolic OH is absent entirely, and its absence has been taken as a criterion for the presence of strong hydrogen bonds.

Mention has been made of the likelihood of the association of phenol through hydrogen bonding. Huggins[6] has cited evidence for the existence of weak additive compounds between phenols and ketones and between phenols and cyclic ethers which he attributes to hydrogen bridges.

[6] M. L. Huggins, J. Organic Chem. **1**, 407 (1936).

It was the purpose of the present study to investigate through measurements of absorption spectra the possibility of the formation of intermolecular hydrogen bonds between phenol molecules, also between phenol molecules and those of certain oxygenated substances. The method used was essentially the same as that used for the study of alcohols.[2, 4] Observations were made upon the fundamental vibrational band of the OH group for different concentrations of phenol in the several solvents.

A 60° rocksalt prism of 7 cm face was used. To increase the dispersion of the instrument the light was caused to pass through the prism

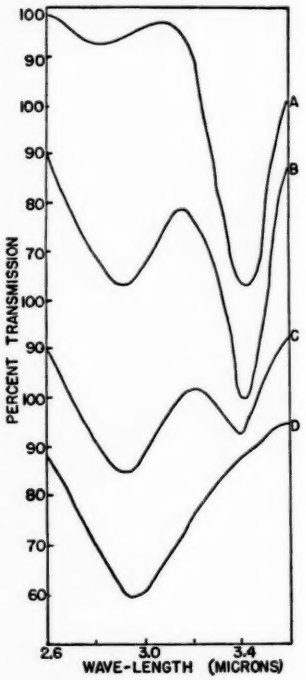

FIG. 4. Percentage transmission of phenol in ethyl acetate: *A*, pure ethyl acetate, cell thickness 0.007 cm; *B*, phenol 0.23 mole/lit., cell thickness 0.007 cm; *C*, phenol 0.95 mole/lit., cell thickness 0.003 cm; *D*, phenol 8 mole/lit., cell thickness 0.001 cm.

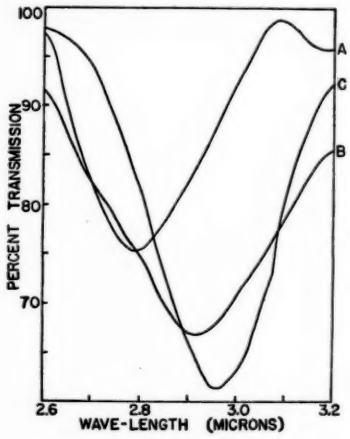

FIG. 5. Ratio of the transmission of a 0.007 cm layer of 0.23 mole/lit., solution of phenol to that of an equally thick layer of the pure solvent: *A*, phenol in benzene: *B*, phenol in ethyl acetate; *C*, phenol in dioxane.

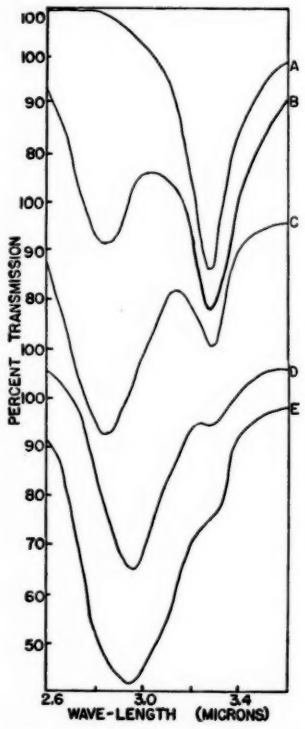

FIG. 6. Percentage transmission of phenol in nitrobenzene: *A*, pure nitrobenzene, cell thickness 0.007 cm; *B*, phenol 0.32 mole/lit., cell thickness 0.007 cm; *C*, phenol 1.2 mole/lit., cell thickness 0.003 cm; *D*, phenol 6 mole/lit., cell thickness 0.001 cm; *E*, phenol 9 mole/lit., cell thickness 0.001 cm.

twice. Instruments of the type used have been previously described.[7] Cell windows were of rocksalt; the thickness of the absorbing layer was maintained by mica washers. In order to bring out the OH band the cell thickness was increased as the phenol concentration was decreased. The maximum thickness was used in obtaining comparison curves of the pure solvents. At each setting of the prism circle, galvanometer deflections were taken with the cell in and with the cell out of the beam, the latter reading being made with a rocksalt plate in the beam to compensate for any scattering or absorption of the cell windows.

The results obtained for phenol in benzene are given in Fig. 1. The bottom curve represents the transmission of the most concentrated solution, 8 mole/lit. In this curve there appears a strong band with maximum of absorption at about 2.96μ, and this we attribute to the OH of the phenol. The less intense band, at 3.28μ, is characteristic of the CH group. For the 5 mole/lit. solution, second curve from the bottom, the positions of the bands apparently have not changed although the ratio of their intensities has changed. The vibrational band of the CH group of the solvent, benzene, appears at approximately the same position as the phenolic CH band. Therefore the band at about 3.28μ would not be expected to decrease with the phenol concentration as does the OH band. Actually the CH band is stronger for the lower concentrations because of the increase in cell thickness. The OH band for 0.95 mole/lit. seems to be double, with one component appearing at the usual position of 2.96μ and the other at shorter wave-lengths. The curve for 0.23 mole/lit. shows

[7] D. S. McKinney, C. E. Leberknight, and J. C. Warner, J. Am. Chem. Soc. **59**, 481 (1937); W. Dahlke, Zeits. f. Instrumentenk. **57**, 18 (1937).

only one maximum, which is at 2.79μ approximately. Diluting the solution has apparently effected a shift to the shorter wave-lengths of some 0.17μ in the OH band. The top curve, which is for pure benzene, indicates that the solvent has no band that would cause falsification by overlapping the hydroxyl band. Fig. 2 shows that the OH band varies in a similar way when the solvent is bromobenzene. It is not likely that bromine is able to share the proton with the oxygen of the OH,[1] and benzene itself has no donor. Hence, neither of the above solvents would be expected to form hydrogen bridges with the solute. The shift of the OH band to the shorter wave-lengths no doubt indicates the breaking of hydrogen bonds between the phenol molecules, the band at 2.96μ being caused by the associated OH and that at 2.79μ by the OH of single molecules.

One may expect the formation of hydrogen bonds with the OH to decrease the binding force between the H and O and hence to effect a shift of the OH band to the longer wave-lengths. The shift reported here for phenolic OH is hardly as great as that observed for alcoholic OH in carbon tetrachloride solution;[2] this difference suggests that the bonds between the phenol molecules are slightly weaker.

If the hydrogen bridges between phenol molecules are not as strong as the corresponding bridges between alcohol molecules, the breaking of the bridges in phenol may be expected to occur at higher concentrations. Lassettre[1] has pointed out that a small amount of hydrogen-bond-forming compound in the solvent materially decreases the polymerization of solutes associated through hydrogen bridges. Thus a small amount of water in the solution may affect measurably the concentration at which single molecules occur. The same is true for the measurements which have been made on alcohols. It should be mentioned that at the time the measurements which are reported here were taken high humidity made it impossible to prepare the solutions and cells without allowing some water to enter the solution, although special precautions were taken to prevent it. Such factors necessarily make measurements of this type somewhat qualitative.

The variations with dilution of the OH band of phenol in oxygenated solvents differ from that discussed above for the solvents, benzene and bromobenzene. For the most concentrated solutions of phenol in all the solvents, however, the position of the band is approximately the same. Fig. 3 shows the results of a study of a series of solutions of different concentrations of phenol in dioxane. For 0.23 mole/lit., the most dilute solution employed, the position of the band is still very nearly 2.96μ, although the intensity is somewhat greater than it is for the corresponding concentration of phenol in benzene. It does not seem likely that this failure of the OH band to shift to the shorter wave-lengths, as it does when the solvent is benzene, means that the phenol is still highly associated at this concentration. Other measurements[4, 8] indicate that oxygenated solvents like dioxane have a greater tendency to decrease the polymerization of solutes of this type than does benzene. This tendency no doubt is due to the ability of the oxygenated solvents to combine with the solute through the formation of hydrogen bonds. If, when the hydrogen bridges are broken between the solute molecules, similar bridges are formed between the solute and solvent molecules, there may be no measurable effect on the OH band, or there may be a shift of the band to higher or lower frequencies, depending upon the strength of the newly-formed bonds as compared to that of the bridges which were broken between the solute molecules. In any case, however, if hydrogen bonds are formed, the position of the OH band would be at wave-lengths longer than for the OH of single molecules. The band appears at slightly shorter wave-lengths in dilute solution in ethyl acetate, Fig. 4, than it does for the most concentrated solutions, but at wave-lengths longer than for the dilute solution in benzene. Furthermore, as was the case for solutions in dioxane, the band is more intense than for the same concentration in benzene.

In Fig. 5 the absorption curves for 0.23 mole/lit. of phenol in dioxane, in ethyl acetate, and in benzene are compared. The absorbing layer was of the same thickness for all three solutions. Each curve represents the ratio of the transmission of the solution to that of an equal thickness of the pure solvent.

[8] C. J. Wilson and H. H. Wenzke, J. Chem. Phys. 2, 546 (1934).

In dilute nitrobenzene solution, Fig. 6, the phenolic OH band appears at wave-lengths only slightly longer than it does in dilute benzene solution. In view of this fact one may predict that the hydrogen bridges between phenol and nitrobenzene, if indeed they form at all, are rather weak. Some may prefer to think of this, as well as the other cases of hydrogen bonding discussed here, not as the formation of definite complexes but merely as a special orientation of the molecules due to proton attraction.

The writers wish to express their thanks to Dr. H. H. Nielsen for the use of his laboratory facilities and for his constant interest in this work, and to Dr. Alpheus W. Smith for his generous support.

JANUARY, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6

Potential Energy Curve of the Excited State of LiH

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A method developed by Klein has been applied to obtain the potential energy curve of the excited electronic state of LiH (state V). This curve crosses the Coulombic curve of Li^+H^- and indicates dissociation of excited LiH into $Li(^2P)+H$. The effect of this behavior on Mulliken's explanation of the unusual shape of the state V curve is discussed. The interaction of the Li^+H^- and $Li(^2P)\cdot H$ curves at moderately large interatomic distances is larger than Mulliken's estimate.

A PROCEDURE for obtaining the potential curve of a diatomic molecule to a sufficient degree of approximation and without the expenditure of an undue amount of time is highly desirable. The power series expansion in terms of the displacement of the atoms from their equilibrium position converges poorly for even moderately large displacements. While the Morse function is probably a fairly good approximation for most curves, for some abnormal ones, such as the curve considered here, it is useless and attempts to modify it can scarcely be expected to offer much improvement. Other types of potential functions have been suggested, but these frequently involve so many parameters that their applications are limited.

O. Klein[1] has given a semi-graphical method for obtaining the curve of a molecule directly from its observed energy levels. So far as the author is aware, this method has been applied only by Rydberg.[2] Since Rydberg has published no details of the application of the Klein method, it may be appropriate to discuss it somewhat fully.

[1] O. Klein, Zeits. f. Physik **76**, 226 (1932).
[2] R. Rydberg, Zeits. f. Physik **80**, 514 (1933).

Klein derives the following equation on the basis of classical mechanics:

$$S(U,\kappa)=\frac{1}{\pi(2\mu)^{\frac{1}{2}}}\int_0^{I'}(U-E(I,\kappa))^{\frac{1}{2}}dI,$$

in which U is a suitable value of the potential energy of the molecule, $E(I,\kappa)$ represents the energy of vibration and rotation as a function of the action variable I and the quantity κ (equal to $P^2/2\mu$), P is the angular momentum of the molecule, μ is its reduced mass, and I' is that value of I for which $U=E$. As Klein suggests, it is probably a good approximation to replace I and κ by their quantum-mechanical equivalents, $(v+\frac{1}{2})h$ and $(K(K+1)h^2)/(8\pi^2\mu)$. The maximum and minimum values of the interatomic distance for a molecule vibrating with the energy U are then given by

$$r_{1,2}(U)=(f/g+f)^{\frac{1}{2}}\pm f,$$

in which $f=(\partial S/\partial U)$ and $g=-(\partial S/\partial\kappa)$. With r_1 and r_2 known for each of a series of U values, the curve for U as a function of r can be plotted. If the $U(r)$ curve for the rotationless state is wanted, the values $f=(\partial S/\partial U)_{\kappa=0}$ and $g=-(\partial S/\partial\kappa)_{\kappa=0}$ are to be used.

The quantity S for a given value of U and κ is obtained by plotting $(U-E)^{\frac{1}{2}}$ (computed from the set of observed energy levels) against I and then determining the value of the area under the curve by numerical integration. The values of S for a series of values of U with κ constant are plotted against U and the quantity f is found from the slope of this curve at any desired value of U. To get g, the values of S for a particular value of U are plotted against κ and the slope at the desired κ value is measured.

Application to State V of LiH

This method has been applied to the determination of a portion of the potential energy curve of the excited state (state V) of LiH. The excellent data of Crawford and Jorgenson[3] were used. Unfortunately these data do not extend to energy levels high enough to permit the drawing of the curve near the dissociation energy. It was found that the curves of $(U-E)^{\frac{1}{2}}$ against I for $K=0$ and $K=2$ lie so close together even on a large scale plot that simple subtraction of one area from another was not precise enough. Accordingly the difference curve was plotted and integrated for each value of U which was used. The graph of S against κ was found to be a straight line for values of κ corresponding to small values of the rotational quantum number. Therefore $\Delta S/\Delta\kappa$ was substituted for $(\partial S/\partial\kappa)_{\kappa=0}$ in finding g. An error of 5 percent in g produces an error of only 1 percent in the value of r_{max} and of less than 2 percent in r_{min}. An error of 5 percent in f leads to one of 4 percent in r_{max} and of 3 percent in r_{min}. It is believed that the amplitudes of vibration here obtained are correct to within ± 0.03A. For the two highest U values used in constructing the $U(r)$ curve, it appears likely that the r values are about 0.03A too large, since the computed r_{min} values fall to the right of a reasonable extrapolation of the lower part of the left branch of the curve.

Table I.

U (ev)	r_{max} (A)	r_{min} (A)
0.157	3.66	1.76
.189	3.76	1.74
.277	3.99	1.61
.410	4.25	1.51
.471	4.41	1.49
.519	4.47	1.45
.566	4.58	1.44
.614	4.75	1.45
.660	4.94	1.46

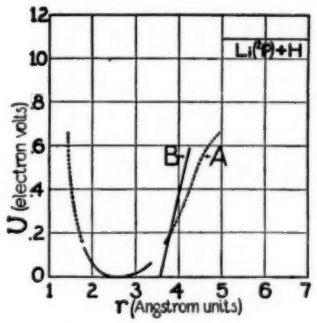

Fig. 1. Dotted part of curve A is portion obtained in present work; solid part is from series expansion of Crawford and Jorgenson (reference 4). Curve B is Coulombic curve of Li^+H^- (reference 5).

Results and Discussion

The results of this application of the Klein method to state V of LiH are summarized in Table I and Fig. 1. The lower, solidly-drawn part of the curve was drawn by use of the series expansion given by Crawford and Jorgenson.[4] The series expansion is most reliable in the region of small vibrational quantum numbers; it has been used here because the Klein method breaks down in just this region due to the small number of energy levels available. It will be observed that the upper and lower parts of the curve fit together excellently.

The chief point of interest about this curve is its unusual shape. It is an exceptionally flat curve which rises on both sides of the equilibrium interatomic distance faster than the osculating parabola. This behavior has been explained by Mulliken[5] as the result of an interaction between two hypothetical unperturbed curves of which one is the Coulombic curve of Li^+H^-. This interaction was considered to be of such a nature that the resultant state V curve should not cross the Coulombic curve but should approach it asymptotically for moderately large values of r, as illustrated in Fig. 1 of reference 5. In this event the region in which the state V curve and

[3] Crawford and Jorgenson, Phys. Rev. **47**, 932 (1935).

[4] Crawford and Jorgenson, Phys. Rev. **49**, 745 (1936).

[5] Mulliken, Phys. Rev. **50**, 1028 (1936).

the Li^+H^- curve reach the same slope should furnish the basis for an estimate of the dissociation energy of the normal state, since the energy difference between states V and N is known precisely from the spectroscopic data. From a rough estimate of the point at which the slope of the state V curve is closest to that of the Coulombic curve, the state N curve should be lifted with respect to its asymptote by about 0.2 ev above Mulliken's estimate of its position. This would make the dissociation energy of normal LiH about 2.3 ev.

According to the present computations, however, the state V curve is flatter at moderately large r values than Mulliken supposed, and must actually cross the Li^+H^- curve, apparently going to $Li(^2P)+H$. If Mulliken's value of 0.75 ev for the height of the state V curve above $Li(^2S)+H$ is accepted as a reasonable estimate, the crossing point is in the neighborhood of 3.8A. This shows that the interaction of the Li^+H^- curve with the unperturbed $Li(^2P)\cdot H$ curve is much more intense near 5A than is indicated by Fig. 2 of reference 5, so that state V dissociates quite definitely into $Li(^2P)+H$. Aside from this quantitative change at large r values, the present results give no reason for altering Mulliken's interpretation of the nature of state V. The position of the Coulombic curve seems to make it unavoidable that state V be predominately of Li^+H^- character over a range of moderately large r values before it goes over into $Li(^2P)+H$.

These conclusions, unfortunately, do not help to fix a precise value of the dissociation energy of the normal state, a quantity which is particularly interesting because the values proposed for it are considerably below that required by Pauling's additivity rule.[6] The value of 2.5 ev adopted by Mulliken is still a reasonable one and is compatible with the portion of the potential energy curve which has here been obtained. But the basis on which this value was reached has been made less certain. It may be said, however, that from the rate at which the state V curve beyond its inflection point is bending, a value less than 2.6 ev is more likely than a larger one.

I wish to record my thanks to Professor Mulliken for many valuable discussions.

[6] Pauling, J. Am. Chem. Soc. **54**, 3570 (1932). This situation is discussed by Mulliken in reference 5.

JANUARY, 1938 JOURNAL OF CHEMICAL PHYSICS VOLUME 6

The Low Temperature Heat Capacity of Gaseous Ethane

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The heat capacity of ethane has been determined at 163° and 143°K by the "hot wire" method and has been found not to level off as suggested earlier by Eucken and Weigert. This speaks against free interval rotation in ethane molecules.

SOME time ago Eucken and Weigert[1] employed the "hot wire" technique, devised by Schleiermacher[2] and since used repeatedly by others, to measure the heat capacity of ethane down to very low temperatures. The most significant result of this work was the observation that at the lowest temperature studied, *ca.* 140°K, the heat capacity curve of ethane gave indications of leveling off appreciably above the classical value, $3R$, for the heat capacity due to rotation and translation. Quantum statistical calculations of Teller and Weigert[3] showed that this behavior was to be expected if only a small hindrance to free internal rotation of the methyl groups in ethane was postulated. Eucken and Weigert concluded that a restraining potential of *ca.* 300 cal./mole fitted their observations best, meaning that at room temperature the methyl groups in an average ethane molecule are freely rotating.

[1] Eucken and Weigert, Zeits. f. physik. Chemie **B23**, 265 (1933).
[2] Schleiermacher, Wied. Ann. **26**, 287 (1886).
[3] Teller and Weigert, Nachr. Götting. Ges. 218 (1933).

Eyring[4] treated the problem of internal rotation in ethane by approximate methods of quantum mechanics (taking into consideration interactions of pairs of electrons but neglecting all higher approximations) and likewise concluded that a potential barrier (restraining potential) of about 300 cal./mole exists.

Measurements of the thermal equilibrium between ethane, ethylene and hydrogen at higher temperatures have been available for some time.[5] When the heat of hydrogenation of ethylene was determined in this laboratory,[6] it became possible with the help of statistically calculated entropies to examine the internal consistency of the data. This was done by Smith and Vaughan[7] and more carefully by Teller and Topley,[8] but all arrived at the same conclusion that the thermochemical and equilibrium data were irreconcilable if the Eucken internal potential was adopted in the calculation of the entropy of ethane. Smith and Vaughan concluded that the statistical entropy calculations were in error due to the assumption of practically free rotation in ethane. Teller and Topley chose, however, to consider the calorimetric value in error. A check from this laboratory[9] demonstrated the correctness of the published figure of the heat of hydrogenation of ethylene, while Rossini[10] obtained a practically identical value from heats of combustion. Thus no doubt can remain that the calorimetric value of the heat of reaction is correct.

It is, of course, possible that the equilibrium measurements are misleading, but the correction required to account for the above discrepancy amounts to a factor of 2 to 3 in the equilibrium constant. Although methane and therefore some olefins other than ethylene are formed to some extent as by-products of the dehydrogenation of ethane[11] (cf. the paper by Pease[5]) the excellent agreement of four available sets of equilibrium measurements indicates that an error of such magnitude is highly improbable. It is to be noted that some of the published measurements have been performed on the homogeneous reaction, others on the heterogeneous process which was accelerated by several catalysts; together they cover a wide temperature and pressure range. One is led, therefore, to the conclusion that the equilibrium measurements are not in error.

Indeed, Howard,[12] in his analysis of the normal coordinate problem of ethane-like molecules, arrived at the conclusion that the rotational structure of the infrared bands of ethane can be explained only if a restraining potential of *at least* 2000 cal. exists in this molecule.

Important additional evidence against the existence of nearly unhindered rotation in ethane was obtained by Witt and Kemp[13] in their study of the heat capacity of solid and liquid ethane at low temperatures. Kemp and Pitzer[14] pointed out that the third law entropy of ethane derived from these measurements is considerably lower than that calculated statistically for the model with the Eucken restraining potential. It is true, of course, that in several well-known instances the observed entropy has been found too low because of imperfect reversibility of the heat capacity measurements at very low temperatures, either within the range covered in the calorimeter or in the extrapolation to the absolute zero; but in the case of ethane no reasons have been advanced to justify the assumption of such errors. Statistical calculations of Kemp and Pitzer reproduce the value of Witt and Kemp, if *ca.* 3100 cal. is assumed for the internal restraining potential in ethane; then the thermal equilibrium measurements become consistent with the measured heat of hydrogenation and the heat capacity of gaseous ethane at higher temperatures[8, 14] falls on the statistical heat capacity curve.

Therefore, little doubt can be left that ethane does not possess the free rotation postulated by Eucken. The present contribution advances the evidence further by showing that the heat

[4] Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).
[5] (a) Pease and Durgan, J. Am. Chem. Soc. **50**, 2715 (1928). (b) Frey and Huppke, Ind. Eng. Chem. **25**, 54 (1933). (c) Travers and Pearce, J. Soc. Chem. Ind. **53**, 322T (1934). (d) Videnski and Vinikova, J. Gen. Chem. Moscow **4**, 120 (1934).
[6] Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 65 (1935).
[7] Smith and Vaughan, J. Chem. Phys. **3**, 341 (1935).
[8] Teller and Topley, J. Chem. Soc. 876 (1935).
[9] Kistiakowsky and co-workers, J. Am. Chem. Soc. **58**, 137 (1936).
[10] Rossini, Nat. Bur. Stand. J. Research **17**, 629 (1936).
[11] Private communication from Dr. Louis S. Kassel.
[12] J. B. Howard, J. Chem. Phys. **5**, 451 (1937).
[13] Witt and Kemp, J. Am. Chem. Soc. **59**, 273 (1937).
[14] Kemp and Pitzer, J. Am. Chem. Soc. **59**, 276 (1937).

capacity curve of gaseous ethane at low temperatures does not level off as the data of Eucken and Weigert suggested.

No method exists at present which is capable of determining directly the heat capacity of gases at low pressures. Despite its several objectionable inherent weaknesses, the "hot wire" method was used in the present work because of the low vapor pressure of ethane at the temperatures of interest.

According to Knudsen,[15] the heat loss per unit area from a thin wire suspended in a cylindrical vessel filled with a gas at such a low pressure that the mean free path of gas molecules is large compared to the diameter of the vessel, is given by:

$$\Delta Q=\frac{1}{(6\pi)^{\frac{1}{2}}}\cdot n\cdot\bar{w}\cdot\alpha[2R+(C_v-3/2R)]\cdot\Delta T, \quad (1)$$

where n is the number of molecules per cc, $\bar{w}$ is the mean molecular velocity, C_v is the heat capacity of the gas, ΔT is the temperature difference between the wire and the walls of the vessel, while α is the accommodation coefficient of the gas on the surface of the wire. This coefficient must be introduced because, according to Knudsen, the gas molecules do not reach thermal equilibrium with a solid surface upon their first collision with it, so that the observed heat conductance is smaller than that calculated without the accommodation coefficient.

Numerous investigations, which we shall not discuss, have shown that the accommodation coefficient depends on the nature of the solid surface and on the nature of the gas, and also on the temperature. It ranges from unity to less than 0.1. A survey of this work indicates that the accommodation coefficient usually decreases with increasing temperature, but at high temperatures begins to rise again, although exceptions to this behavior have been observed.

Because of the uncertainty of the accommodation coefficients, measurement of heat conductance by the gas gives only a lower limit of the heat capacity, and does not in general reproduce correctly even its temperature dependence. Eucken and Weigert's procedure in eliminating the objectionable accommodation coefficient consisted in measuring first the heat conductances of two gases (argon and ethane) at temperatures so high that reliable data on the heat capacities of both could be secured by other methods. By forming the ratio of Eqs. (1) for the two gases and substituting their heat capacities, a ratio of accommodation coefficients was calculated which, experimentally, showed a tendency to approach unity with decreasing temperature. For the purposes of extrapolation to low temperatures, at which the heat capacity of only one gas was known, it was assumed that the ratio did actually approach unity. The heat capacity of the other gas was then readily calculated.

[15] M. Knudsen, Ann. d. Physik **34**, 593 (1911).

Experimental Details

The general principle of the method of Eucken and Weigert has been adopted for the present experiments, but some modifications were introduced. Since the accommodation coefficient depends rather decisively on the structure of the solid surface, an apparatus was constructed which contained four different wires, with the hope that the average of measurements on all would give more reliable results. Three of the wires selected were the usual blank drawn platinum wires: the first as supplied by the manufacturer (0.02 mm diameter); the second wire was electrolytically coated with an active deposit of platinum black and the third was electrolytically coated with a coarse porous deposit of nickel, and later oxidized in air by heating. The fourth wire was a blank drawn nickel wire oxidized in air. Thus, of the four surfaces two were metallic, one relatively smooth, the other decidedly irregular; two were coated with oxide, one smooth and the other rough.

The thin wires (H, Fig. 1), *ca.* 20 cm in length, were mounted co-axially in cylindrical holes (1 mm diameter) drilled in brass rods *ca.* 10 mm in diameter (R). One end of the wire was soldered to the rod, the other passed through a narrow hole in a thin mica plate (m) mounted at the end of the rod and was held under gentle tension by an insulated tungsten spring (s). Very near the mica plate two heavier wires (W) were fused to the thin wire. This entire unit was sealed in a glass tube (G) of a diameter somewhat

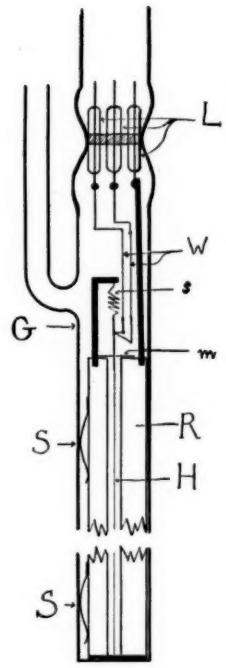

FIG. 1.

larger than that of the brass rods. The latter were pressed against the glass walls by suitable springs (*S*). A wire from the brass rod and the two fused to the end of the heater wire were connected with the outside by means of tungsten-in-glass seals (*L*). Direct measurements showed that the temperature of the brass rods was less than 0.02°C above that of the outside of the glass tube when the heater wire was heated as in experiments to be described. This agrees with calculations which consider the diameter of the wire, of the brass rod and the heat conductance by the gas.

The glass tubes containing the wires were joined to a thermostated 5-liter flask, which communicated with a thermostated system of gas pipettes for admitting accurately measured small amounts of various gases into the system. The flask was also connected through a large stopcock with a fast pumping system. Apiezon stopcock grease was used throughout. A Pirani gauge, constructed as the other units, was attached to the system and kept in an ice bath.

The "hot wires" were placed in a large Dewar cylinder provided with a stirrer, a small electric heater and liquid-filled temperature regulator. The regulator, as well as the Dewar vessel, was filled with the light fraction of the "gas-machine" gasoline, b.p. below 40°C. The cooling agent (solid carbon dioxide or liquid air) was contained in a double-walled glass cylinder mounted within the larger Dewar vessel. The interspace of the cooling vessel was permanently connected to a mercury vapor pump, the fore-vacuum side of which was closed from the oil pump, during the experiments. A by-pass from the fore-vacuum side of the pump to the interspace led through a fine needle valve, provided with sylphon bellows instead of packing. The valve was driven by reversible Telechron motor, the two coils of which were attached to the two poles of a relay operating also the heating element in the large Dewar vessel.

This arrangement operates in such a way that when the heater is on, the Telechron motor turns in a direction which slowly closes the valve so that the mercury pump reduces the gas pressure in the interspace between the cooling agent and the thermostat liquid. The heat conductance between them therefore gradually decreases. The reverse process is taking place with the heater off. When a perfect balance of heat flow has been obtained, the valve executes small symmetric oscillations around a fixed position, since the heater is half of the time on and half of the time off. But when the heat balance has been disturbed (as for instance by a loss of the cooling agent) and the heater is, let us say, most of the time in the off position, the valve begins to execute unsymmetric oscillations, the trend being on the average to open it more, thus admit more gas to the interspace and thereby increase the heat conductance. This process continues until the heat balance has been re-established and the heater is again operating in the most favorable manner, being half of the time off and half on. Thus it is possible to delay refilling the cooling agent for longer times and yet have the cryostat operate at a constant temperature without measurable drifts. Regular variations were found to amount to at most 0.03°, but improvements in the regulator design could easily reduce this further.

The temperatures were measured with a 5-junction copper-constantan thermel, a correction to the I.C.T. thermal e.m.f. data being

determined at the oxygen and solid carbon dioxide points and at the transition temperature of $Na_2SO_4 \cdot 10H_2O$.

The electrical system consisted of a Mueller type L. & N. bridge operated from a large 12-volt storage battery through variable resistances; because of the three wire connections only the resistance of the thin portions of the "hot wire," within the 1 mm holes, was measured. In series with the wires was a standard resistance across a type K, L. & N. potentiometer, used also to measure the e.m.f. of the thermel.

The procedure during a typical run consisted in evacuating the system to better than 10^{-5} mm Hg, while the cryostat was being cooled to the desired temperature. The resistance of the wires at the cryostat temperature was determined by extrapolating their resistance to zero heating current. Thereupon the current was increased until the temperature of the wires was 20° higher. The current was determined by measuring the potential drop across the standard resistance and the square of it gave a relative measure of the heat losses by radiation and by end conduction. Then the system was flushed two or three times with the gas and filled to a fixed pressure, and the current needed to keep the wire at the same temperature was determined. Most of the measurements were made with the same pressure of 3.2×10^{-2} mm, but a few measurements made at different pressures gave the same values of the accommodation coefficients. The difference of the square of the current with and without the gas gave a relative measure of the heat conducted by the gas. The system was evacuated and the entire procedure repeated with another gas, care being taken that exactly the same amount of gas was admitted and that the temperature of the wire remained unchanged.

The Results and Discussion

Heat conductance by argon, methane, ethylene, ethane, propylene, propane, butene-2 (*trans*) and butene-2 (*cis*) has been determined. For the four last gases no reliable heat capacity data are available as yet. Pending their determination a discussion of their heat conductance will be postponed.

Table I illustrates the method of calculating the results from the observed values of the potential across the standard resistance. Since the temperature, and therefore the resistance of the wires, remains constant during all measurements, and the gases are at the same concentration, ΔT and n drop out of the equation (1) when the ratio of two heat conductances if formed:

$$\frac{\Delta Q''}{\Delta Q'} = \frac{(M')^{\frac{1}{2}}}{(M'')^{\frac{1}{2}}} \cdot \frac{[2R+(C_v''-3/2R)]}{[2R+(C_v'-3/2R)]} \cdot \frac{\alpha''}{\alpha'} \quad (2)$$

Table I. *Methane and ethylene. Temperature of the bath, 273.10°K. Temperature of the wires, 293.10°K.*

	(Pt) I	(Ni $-Ni_2O_x$) II	(Pt $-$Pt bl.) III	(Pt $-Ni_2O_x$) IV
Resistance at 293° in ohms	37.980	30.630	37.125	33.930
Vacuum e^*	0.0418	0.0871	0.0907	0.1120
Methane E''^*	0.1513	0.1916	0.1857	0.2189
Ethylene E'^*	0.1503	0.1888	0.1812	0.2146
$\frac{\Delta Q''}{\Delta Q'} = \frac{E''^2-e^2}{E'^2-e^2}$	1.014	1.037	1.067	1.056
Experiment repeated two days later				
e^*	0.0423	0.0876	0.0913	0.1123
E''^*	0.1513	0.1918	0.1857	0.2190
E'^*	0.1505	0.1891	0.1814	0.2149
$\frac{\Delta Q''}{\Delta Q'} = \frac{E''^2-e^2}{E'^2-e^2}$	1.013	1.037	1.064	1.053
Average	1.013	1.037	1.065	1.055
C_v' ethylene (283.1)	8.02			
C_v'' methane (283.1)	6.44			
from Eq. (2) α''/α' (283.1)	0.929	0.950	0.977	0.968

* Potential across standard resistance.

To calculate the ratio of accommodation coefficients from (2) the heat capacities of the two gases must be known. The following values have been used:

For argon the value $\frac{3}{2}R$ was used throughout.

The heat capacity of methane was taken from Eucken and Bertram[16] and for the lowest temperatures was calculated statistically.

For ethylene, the values given by Eucken and Parts,[17] were used. For the lower temperatures a statistical calculation using the frequencies given by Bonner[18] was made, assuming classical rotation and a rigid rotator-harmonic oscillator model.

The heat capacity of ethane from 303 to 193°K was taken from Eucken and Parts; graphical interpolation was used and the figures reduced to ideal gas state.

The accommodation coefficient ratios, calculated in the manner shown in Table I, have been collected in Table II. Each of the values there given is the average of two independent determinations, the deviations from the mean being never larger than 0.4 percent but usually considerably less.

Several rather instructive facts emerge upon the study of Table II. Eucken and Bertram[16] contend that the nickel-nickel oxide wire is exceptionally favorable in giving accommodation coefficient ratios near unity. The table shows that the differences between the several surfaces used are extremely small and that, if anything, the platinum black surface is the best one from this point of view. The absolute values of the accommodation coefficient ratios are lower throughout than those of Eucken. This may be due to a differently conditioned surface but perhaps also to the circumstance that Eucken's method does not completely eliminate the radiation correction, as may be done when the wire is maintained throughout at the same temperature.

There appears to be no advantage in using argon as done by Eucken for the reference gas since the accommodation coefficient ratios in this case show a particularly pronounced temperature variation.

TABLE II. *Ratios of the accommodation coefficients.*

	T°K	I (Pt)	II (Ni − Ni_2O)	III (Pt − Pt bl.)	IV (Pt − Ni_2O)
CH_4/A	283	0.845	0.848	0.900	0.880
	243	0.876	0.895	0.921	0.910
	223	0.888	0.905	0.920	0.915
	195	0.905	0.919	0.931	0.925
CH_4/C_2H_4	283	0.929	0.950	0.977	0.968
	243	0.932	0.955	0.982	0.972
	223	0.930	0.953	0.975	0.970
	195	0.936	0.952	0.977	0.972
	163	0.931	—*	—*	0.957
	143	0.950	—*	—*	0.989
C_2H_6/C_2H_4	303	1.011	1.030	1.009	1.016
	283	1.005	1.016	1.002	1.010
	243	1.002	1.013	1.002	1.005
	223	1.013	1.012	1.001	1.002
	193	1.005	1.009	1.005	1.007

* Units broken.

The ratio of the accommodation coefficients of methane to ethylene, which is essentially independent of temperature in the range from 283 to 163°K, shows a sudden rise at 143°K. A probable explanation of this peculiar behavior was discovered through measurements of the pressure of gas admitted to the system with the "hot wire" vessels immersed in liquid oxygen. At higher temperatures the pressure of each gas was found to be the same when admitted to the system from the same pipette at a fixed pressure, whereas at the temperature of liquid oxygen it was found that the pressure of methane was appreciably higher than that of the other gases. (See Table III.)

It is evident, therefore, that ethylene and ethane are adsorbed in greater amounts on the cold parts of the system than is methane. Probably this polymolecular film adsorption[19] starts at 143°K, producing a slightly lower pressure of ethylene in the system and thus simulating an abnormally high accommodation coefficient of methane.

TABLE III. *Pressures at liquid oxygen temperature.*

	METHANE	ETHANE	ETHYLENE
mm Hg	1.25×10^{-2}	0.95×10^{-2}	0.95×10^{-2}

[16] Eucken and Bertram, Zeits. f. physik. Chemie **B31**, 363 (1936).

[17] Eucken and Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).

[18] Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

[19] Because of the large volume of the system a unimolecular film adsorption in the "hot wire" tubes does not affect the gas pressure significantly.

Of great importance for the following is that even at liquid oxygen temperature the residual pressures of ethane and of ethylene are the same; hence, these two gases are adsorbed in equal amounts; the same undoubtedly is true at the temperature of 143°K, when the total adsorption is still quite small.

As Table II shows, the accommodation coefficient ratios of ethane to ethylene are very near unity at all temperatures and on all wires. A small temperature trend does exist, which in all instances seems to bring the ratios nearer unity with decreasing temperature. But in any case an extrapolation over some 50° to 143°K should introduce no significant uncertainties. Table IV shows the selected figures of the ratios of the accommodation coefficients, as well as the heat capacities of ethane deduced therefrom.

The heat capacity of ethane, as determined here and as given by Eucken and Weigert, has been plotted in Fig. 2. The new data show no evidence of the leveling off of the C_v curve above 7 cal./mole as was suggested by the lowest point of the Eucken and Weigert measurements. Instead, a steady decrease is observed, the points falling on the curve calculated by Dr. Pitzer for an internal restricting potential of 3100 cal. with the unknown vibrational frequency of ethane being taken as 1100 cm^{-1}. This selection agrees well with the calculation of Howard[12] (1000 cm^{-1}) based on the normal coordinate treatment of ethane. We are indebted to Dr. Pitzer for the permission to use the curve.

TABLE IV.

$\frac{T_{therm.}+T_{wire}}{2}$		I	II	III	IV
193°K	α/α meas.	1.005	1.009	1.005	1.007
	C_v ethylene	6.46			
	C_v ethane	8.02			
163°K	α/α extrapolated	1.007	1.005	1.002	1.001
	C_v ethylene	6.15			
	C_v ethane, calc.	7.40	7.45	7.43	7.46
	Average		7.43		
143°K	α/α extrapolated	1.003	—*	1.001	1.000
	C_v ethylene	6.05			
	C_v ethane, calc.	7.11		7.09	7.10
	Average		7.10		

* This unit was broken during this run.

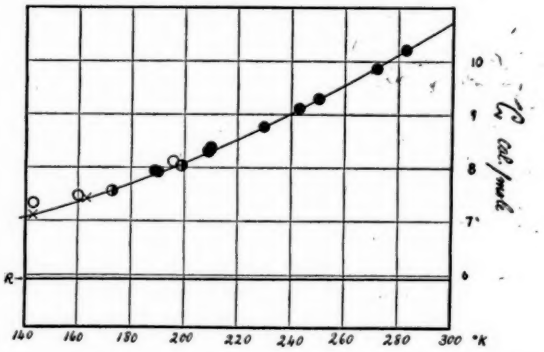

FIG. 2. Dark circles, Eucken and Parts; light circles, Eucken and Weigert; half-darkened circles, Eucken and Bertram; cross, this work; line, theoretical curve of Pitzer, $V_0 = 3100$ cal.

The new data, contributing to the evidence discussed in the beginning of the paper, eliminate the last doubts concerning the existence of a large internal restricting potential in ethane, but they do not make its origin more understandable. Dr. Howard, upon an examination of the quantum-mechanical problem of ethane, informs us that calculations which take into account interactions of pairs of electrons, by the usual approximation methods, lead to only small restricting potentials of the same order of magnitude as deduced by Eyring.[4] The restriction of free rotation around the carbon-carbon single bonds belongs, evidently, to those quantum mechanical problems for which a more refined treatment is needed, than usually given, to obtain an even semi-quantitative agreement with experimental data.

The Thermodynamic Functions of the Chloro- and Bromomethanes, Formaldehyde and Phosgene

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By use of the harmonic oscillator-rigid rotator approximation the free energy function $(F^0-E_0^0/T)$, and the heat content $(H^0-E_0^0)$ of the chloro- and bromomethanes, formaldehyde and phosgene have been calculated from spectroscopic and electron diffraction data over temperature ranges where the aforesaid approximations are valid. The heat capacity C_p for the bromomethanes, formaldehyde and phosgene have been calculated over the same temperature range as the free energy function and the heat content. The entropies of the ten molecules in the hypothetical ideal gas state at 298.1°K have been calculated. With the values of $(F^0-E_0^0/T)$ for β-graphite, chlorine, oxygen and hydrogen tabulated by other investigators with our values of this function for the chloromethanes, formaldehyde and phosgene and the heat data of Bichowsky and Rossini we have calculated the free energy of formation of these molecules.

THE great interest in Raman and infrared spectroscopy in recent years has made available data on the fundamental vibration frequencies of a large number of molecules. This is particularly true of organic molecules. There is little prospect of immediate knowledge of the anharmonicity and vibration-rotation interaction constants becoming available for most polyatomic molecules. These data taken with the moments of inertia calculable from electron diffraction data on structures is sufficient to calculate the thermodynamic functions of the molecules in the hypothetical ideal gas state to the rigid rotator, harmonic oscillator approximation. The accuracy of calculations to that approximation has been discussed by Mayer, Brunauer and Mayer[1a] and Gordon.[1b, c] Among the halogen methanes only the energy content and heat capacity have been calculated by Vold[2] for the chloromethanes and the entropy of carbon tetrachloride at two temperatures by Lord and Blanchard.[3] It seemed worth while to us to extend the work of Vold to the calculation of the entropy and free energy function of the chloromethanes as well as calculating the heat content, entropy, free energy and heat capacity of the bromomethanes, formaldehyde and phosgene.

The theory and methods of calculating thermodynamic functions from spectral data have been amply summarized by Kassel.[4] This excellent review makes it unnecessary to discuss the methods used further than saying we have used Kassel's Eqs. (65) for calculating the vibrational contributions. For the rotational contributions we have used formulae derivable[5] from Kassel's (49) or (50). When a knowledge of the stretching and anharmonicity constants becomes available the logarithm of the sum, $\sum_i f_i g_i$, (Eq. (63), reference 4) may be added with the proper multiplier to our functions to obtain more accurate values of the quantities in question.

When there are isotopic species of the molecules for which one is calculating the thermodynamic functions it is customary to evaluate the functions for each isotopic species and take a weighted mean as the value of the function for the naturally occurring mixture.[6, 3, 4] For diatomic molecules of the type $A_2^{m_1}$, $A^{m_1}A^{m_2}$ and $A_2^{m_2}$ one can show that only a small error is made by taking chemical atomic weights and average frequencies in calculating the values of the partition functions. If the relative abundance of A^{m_1} is "a," then the average molecular weight is $(am_1+(1-a)m_2)$, the average moment of inertia is $1/2(am_1+(1-a)m_2)e^2$, (d the nuclear

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[1] (a) Mayer, Brunauer and Mayer, J. Am. Chem. Soc. **55**, 50 (1933); (b) Gordon and Barnes, J. Chem. Phys. **1**, 692 (1933); (c) Gordon, ibid. **2**, 65 (1934).
[2] Vold, J. Am. Chem. Soc. **57**, 1192 (1935).
[3] Lord and Blanchard, J. Chem. Phys. **4**, 707 (1936).
[4] Kassel, Chem. Rev. **18**, 277 (1936).
[5] Fowler, *Statistical Mechanics*, Chapters 5 and 6 (Cambridge Press, 1936).
[6] Giauque and Overstreet, J. Am. Chem. Soc. **54**, 1731 (1932).

TABLE I. *The entropy of CCl_4 at 298.1°K.*

Lord and Blanchard[3]	74.05 E.U.
This research	74.17 E.U.

separation), and the average frequency is $(1/2\pi)(2k/(am_3+(1-a)m_2))^{\frac{1}{2}}$ where k is the force constant. Substitution of these values in the partition functions, $f_{\text{trans}}(T)=(2\pi mkT/h^2)^{\frac{3}{2}}V$, $f_{\text{rot}}(T)=8\pi^2IkT/h^2$ and $f_{\text{vib}}(T)=kT/h\nu$,[7] and comparing with the weighted averages shows that the error made is less than $((m_2-m_1)/m_1)^2$ in each partition function. For chlorine with isotopes 35 and 37 this would be an error of less than 0.4 percent in each partition function or less than 0.03 E.U. in the entropy. We have used this simplification throughout our calculations on molecules containing chlorine and bromine. A comparison of our value for the entropy of carbon tetrachloride at 298.1°K with that of Lord and Blanchard indicates the accuracy of carrying this approximation over to polyatomic molecules. (See Table I.)

The use of the symmetry number has been discussed in several papers.[1, 3, 6, 8] Following Giauque and Overstreet[6] we have ignored the existence of isotopic molecules in choosing the symmetry number for the various molecules considered. The symmetry numbers used are given in Table II.

THE HALOGEN METHANES

The frequencies given by Sponer[9] for the chloro- and bromomethanes were used in calculating the vibrational contribution to the various thermodynamic functions. The frequency $\delta_t' \parallel$ is not given by Sponer. Kohlrausch[11] gives 1054 cm^{-1} for this frequency. In the case of methylene bromide two frequencies are missing in Sponer's tabulation. From the more recent work of Gockel,[10] Kohlrausch[11] and Trumpy[12] we have taken the vibrations $\delta_t' \parallel$ and $\delta^2 \perp$ to be 806 and 487 cm^{-1}, respectively.

TABLE III.

C−Cl = 1.76A	C−Br = 1.91A	C−H = 1.09A
∠H−C−H = 111°	∠Cl−C−Cl = 112°	CH_2Cl_2 and $CHCl_3$
In methylene bromide	∠Br−C−Br = 111°	
In bromoform	∠Br−C−Br = 112°	

The internuclear distances and bond angles were taken for the chloromethanes from the review paper of Brockway.[13] These constants for the bromomethanes were taken from the recent publication of Levy and Brockway.[14] A slight distortion of the hydrogen-carbon-hydrogen angle from the tetrahedral angle in the direction to be expected from electrostatic repulsion was assumed for the methyl and methylene chlorides and bromides. This assumption is practically without effect on the moments of inertia so calculated. Table III gives the values we have used.

The calculations for molecules with several low frequencies were not carried to as high temperatures as were those for the molecules all of whose frequencies were reasonably large. The lack of the anharmonicity corrections would make high temperature calculations for the

[7] The classical limiting form of the vibrational partition function is assumed here for simplicity.
[8] Gordon and Barnes, J. Phys. Chem. **36**, 2601 (1932).
[9] Sponer, *Molekulspektren*, Vol. I, Table 14 (Springer, 1935).
[10] Gockel, Zeits. f. physik. Chemie **B29**, 87 (1935).
[11] Kohlrausch, ibid. **B29**, 288 (1935).
[12] Trumpy, Zeits. f. Physik **100**, 250 (1936).
[13] Brockway, Rev. Mod. Phys. **8**, 231 (1936).
[14] Levy and Brockway, J. Am. Chem. Soc. **59**, 1662 (1937).

TABLE II. *The frequencies of the chloro- and bromomethanes used.*

	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	CH_3Br	CH_2Br_2	$CHBr_3$	CBr_4
$\nu_t^1 \parallel$	732 cm^{-1}	2985 cm^{-1}	3018 cm^{-1}	459 cm^{-1}	610 cm^{-1}	2988 cm^{-1}	3021 cm^{-1}	265
$\nu_t^2 \parallel$	2900	700	667	775[3]	2900	576	539	667[3]
$\nu' \perp$	3047[2]	3049	760[2]		3061[2]	3060	654[2]	
$\nu^2 \perp$		738				636		
$\delta_t^1 \parallel$	1355	1054	366	313[3]	1305	(806)	222	183[3]
$\delta_t^2 \parallel$		284				174		
$\delta^1 \perp$	1020[2]	1153	1216[2]		957[2]	1090	1144[2]	
$\delta^2 \perp$	1460[2]	899	260[2]	217[2]	1450[2]	(478)	154[2]	123[2]
δ		1417				1390		
σ	3	2	3	12	3	2	3	12

The superscripts on the frequencies are the degeneracies of the vibrations.

molecules with several low frequencies quite uncertain.

Formaldehyde and Phosgene

Table IV gives the frequency assignments used for formaldehyde and phosgene. The formaldehyde values are from Sponer.[9] The frequency, $\nu_t'\,||$, using the designation of Sponer, has been displaced upward by an interaction with $2\delta_t\,||$, and should be somewhat lower than 2970. If the identification of Sponer for $\nu_t\,||$ and $2\delta_t\,||$ are reversed, $\nu_t'\,||$ has been displaced downward and should be higher than 2780. We have used the round figure 2900 cm^{-1} since even at 1500°K this frequency contributes only 0.065 cal. per °K per mole to the free energy function. The Raman frequencies used for phosgene are those given by Ananthakrishnan.[15] The agreement between his data and those of Dadieu and Kohlrausch[16] is very good. Only five frequencies have been observed for phosgene. The calculations were made using only those five frequencies. The missing frequency ($\delta\perp^1$ or $\delta\perp^2$) would probably be not less than 300 cm^{-1} if the difference between these two frequencies in formaldehyde and in methylene chloride can be used as a guide. The values of $(F^0-E_0^0/T)$ would be high by $0.25R$ cal. per mole per °K at 298°K and high by $0.64R$ at 600°K if this frequency were 300 cm^{-1}. This would amount to an error of 1 percent at 298°K and 2 percent at 600°K. When a value for this frequency is determined the necessary corrections in our tabulated values can be easily made by use of the tables of Gordon and Barnes.[17]

A third law calculation of the entropy of phosgene taken with our calculation of its entropy with one frequency missing could be used to fix the magnitude of the unknown frequency. The heat capacities tabulated in Table IX together with equation of state data and measured gaseous heat capacities offer an alternative method for fixing this frequency. The various measurements of the equilibrium constant for the reaction $CO+Cl_2=COCl_2$,[18] are not sufficiently accurate to determine ΔS to better than about 2 E.U. hence the possibility of determining S_{COCl_2} from equilibrium measurements at the present time is ruled out.

Table IV.

	Formaldehyde	Phosgene
$\nu_t^1\|\|$	2900 cm^{-1}	573
$\nu\perp$	2800	832
$\nu_t^2\|\|$	1744	1807
$\delta_t\|\|$	1461	302
$\delta\perp^1$	1039	442
$\delta\perp^2$	917	

Table V.

H_2CO	$I_A=24.33\times10^{-40}$	$I_B=21.4\times10^{-40}$	$I_C=2.9\times10^{-40}$
Cl_2CO	C−Cl = 1.68A	C−O = 1.28A	∠Cl−C−Cl = 117°

The moments of inertia for formaldehyde were also taken from Sponer.[9] Those of phosgene were calculated from the bond distance and bond angle values of Brockway, Beach and Pauling.[19] Table V gives these constants for formaldehyde and phosgene.

The free energy function and the heat content of formaldehyde and phosgene are given in Table VI. The units and standard state are the usual ones.

In Table VII we have tabulated the entropies of the gases in the hypothetical ideal gas state at 298.1°K.

Table VI.

	H_2CO		Cl_2CO	
	$-\frac{F^0-E_0^0}{T}$	$(H^0-E_0^0)$	$-\frac{F^0-E_0^0}{T}$	$(H^0-E_0^0)$
291.1	45.872	2.364	59.065	2.870
298.1	46.265	2.432	59.299	2.966
350	47.580	2.902	60.930	3.637
400	48.701	3.388	62.343	4.321
500	50.632	4.440	64.835	5.754
600	52.291	5.596	66.984	7.256
700	53.764	6.848	68.886	8.812
800	55.097	8.186	70.595	10.409
900	56.329	9.599	72.150	12.036
1000	57.473	11.078		
1100	58.550	12.616		
1200	59.563	14.202		
1300	60.521	15.830		
1400	61.437	17.498		
1500	62.309	19.198		

[15] Ananthakrishnan, Proc. Ind. Acad. Sci. **VA**, 285 (1937).
[16] Dadieu and Kohlrausch, Mon. f. Chemie **57**, 225 (1931).
[17] Gordon and Barnes, J. Chem. Phys. **1**, 297 (1933).
[18] (a) Bodenstein and Dunant, Zeits. f. physik. Chemie **61**, 437 (1908); (b) Bodenstein and Plaut, ibid. **110**, 399 (1924); (c) Atkinson, Heycock and Pope, J. Chem. Soc. **117**, 1410 (1920).
[19] Brockway, Beach and Pauling, J. Am. Chem. Soc. **57**, 2693 (1935).

TABLE VII.

Substance	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4	CH_3Br
S^0 298.1	55.99	64.68	70.82	74.17	58.74
Substance	CH_2Br_2	$CHBr_3$	CBr_4	H_2CO	Cl_2CO
S^0 298.1	70.84	79.14	85.59	52.42	67.24

THE FREE ENERGY OF FORMALDEHYDE

Bichowsky and Rossini[20] from the data of von Wartenberg, Muchlinski and Riedler[21] estimate for the reaction $C_{\beta g}+H_2+\frac{1}{2}O_2=H_2CO$, $\Delta H_{291}{}^0=-28.48$ Kcal./mole. $(H^0-E_0{}^0)_{291}$ is 0.239 Kcal. for β-graphite,[22] 2.022 Kcal. for oxygen, 1.975 Kcal. for hydrogen and 2.364 Kcal. for formaldehyde. Adding one gets $\Delta E_0{}^0=-27.62$ Kcal./mole.

Newton and Dodge[23] have measured directly the equilibrium constants for $H_2+CO=H_2CO$, (1) and $H_2+H_2CO=CH_3OH$, (2). They give as the best values, $K_1=1.72\times10^{-5}$ (520°K) and $K_2=2.09\times10^{-3}$ (470°K). Using Giauque's[24] value for $(F^0-E_0{}^0/T)$ for hydrogen, Clayton and Giauque's[25] value for CO, and Kassel's[26] value for CH_3OH, it is possible to calculate $\Delta(F^0-E_0{}^0/T)$ for each of these reactions at the temperature at which the equilibrium constants have been determined. Doing so we find for $CO+H_2=H_2CO$, $\Delta(F^0-E_0{}^0/T)_{520}=24.30$, and for $H_2+H_2CO=CH_3OH$, $\Delta(F^0-E_0{}^0/T)_{470}=29.16$. Since $\Delta F^0=-RT\ln K$ and $\Delta E_0{}^0=\Delta F^0-T\Delta(F^0-E_0{}^0/T)$ we have,

$CO+H_2=H_2CO$ $\quad\Delta E_0{}^0=-1.31$ Kcal./mole,

$H_2CO+H_2=CH_3OH$ $\quad\Delta E_0{}^0=-20.38$ Kcal./mole.

Now $C_{\beta g}+\frac{1}{2}O_2=CO$, $\Delta E_0{}^0=-27.40$,[25] and $C_{\beta g}$

[20] Bichowsky and Rossini, *Thermochemistry* (Rheinhold, 1936), p. 45.
[21] Zeits. f. angew. Chemie **37**, 457 (1924).
[22] Landolt-Börnstein, *Tabellen*.
[23] Newton and Dodge, J. Am. Chem. Soc. **55**, 4758 (1933).
[24] Giauque, J. Am. Chem. Soc. **52**, 4826 (1930).
[25] Clayton and Giauque, J. Am. Chem. Soc. **54**, 2610 (1932).
[26] Kassel, J. Chem. Phys. **4**, 493 (1936).

TABLE VIII.

	CH_3Cl		CH_2Cl_2		$CHCl_3$		CCl_4	
T°K	$-\left(\frac{F^0-E_0{}^0}{T}\right)$	$(H^0-E_0{}^0)$	$-\left(\frac{F^0-E_0{}^0}{T}\right)$	$(H^0-E_0{}^0)$	$-\left(\frac{F^0-E_0{}^0}{T}\right)$	$H^0-E_0{}^0$	$-\left(\frac{F^0-E_0{}^0}{T}\right)$	$H^0-E_0{}^0$
291.1	49.43	2.422	56.58	2.765	61.14	3.287	61.95	3.996
298.1	49.63	2.496	57.10	2.859	61.41	3.405	62.28	4.145
350	50.99	3.018	58.68	3.527	63.30	4.244	64.59	5.203
400	52.16	3.573	60.06	4.232	64.96	5.113	66.63	6.282
500	54.22	4.812	62.52	5.781	67.94	6.978	70.29	8.542
600	56.04	6.207	64.71	7.479	70.58	8.972	73.50	10.892
700	57.69	7.741	66.70	9.300	72.95	11.060		
800	59.21	9.343	68.51	11.214	75.10	13.220		
900	60.63	11.158						
1000	61.97	12.998						
1100	63.23	14.926						
1200	64.44	16.923						

	CH_3Br		CH_2Br_2		$CHBr_3$		CBr_4	
	$-\left(\frac{F^0-E_0{}^0}{T}\right)$	$H^0-E_0{}^0$	$-\left(\frac{F^0-E_0{}^0}{T}\right)$	$H^0-E_0{}^0$	$-\left(\frac{F^0-E_0{}^0}{T}\right)$	$H^0-E_0{}^0$	$-\left(\frac{F^0-E_0{}^0}{T}\right)$	$H^0-E_0{}^0$
291.1	52.01	2.467	61.94	3.071	68.01	3.701	70.81	4.728
298.1	52.21	2.544	62.20	3.178	68.32	3.829	71.20	4.893
350	53.60	3.088	63.95	3.936	70.43	4.733	73.91	6.037
400	54.80	3.664	65.49	4.724	72.27	5.657	76.25	7.085
500	56.92	4.943	68.24	6.418	75.55	7.615	80.42	9.560
600	58.79	6.375	70.66	8.233	78.41	9.678	83.95	11.981
700	60.48	7.938						
800	62.04	9.613						
900	63.49	11.391						
1000	64.86	13.257						
1100	66.15	15.199						
1200	67.37	17.208						

TABLE IX. *Heat capacities at constant pressure of ideal gas. cal./mole °K.*

T°K	CH_3Br	CH_2Br_2	$CHBr_3$	CBr_4	H_2CO	Cl_2CO
298.1	10.18	14.25	17.08	21.84	8.90	12.73
350	11.07	15.30	18.09	22.66	9.44	13.40
400	11.96	16.19	18.89	23.24	10.00	13.93
500	13.60	17.60	20.17	24.04	11.07	14.71
600	15.05	18.70	21.10	24.52	12.09	15.32
700	16.27				12.97	15.78
800	17.30				13.77	16.14
900	18.24				14.48	16.42
1000	19.06				15.09	
1100	19.78				15.63	
1200	20.41				16.10	
1300					16.49	
1400					16.84	
1500					17.14	

$+2H_2+\frac{1}{2}O_2=CH_3OH$, $\Delta E_0^0=-45.62$. Thus from the Newton and Dodge K_1 one has, $C_{\beta g}+H_2+\frac{1}{2}O_2=H_2CO$, $\Delta E_0^0=-28.7$ Kcal./mole and from their K_2, $\Delta E_0^0=-25.2$ Kcal./mole. The mean of these two values of ΔE_0^0 is -27.0 Kcal./mole which agrees with the combustion value, obtained in the previous paragraph, within the limits of experimental error of the determination. In calculating the free energy of formation of formaldehyde we have used the unweighted mean of the three independent values of ΔE_0^0 of formation of formaldehyde, -27.2 Kcal./mole. The free energy function for oxygen was obtained from the publication of Johnston and Walker.[27]

In Table VIII we have the free energy function and heat content for the chloro- and bromomethanes tabulated. The standard state is the usual one for statistical mechanical calculations, namely the infinitely dilute gas at 0°K. The hundred degree intervals for which the functions are given are sufficient for graphical interpolation. The units are kilocalories per mole per degree or per mole as the case may be.

Using the Bichowsky and Rossini[20] values for the heats of formation of the chloromethanes one obtains the following value for ΔE_0^0 of formation of the gaseous chloromethanes. CH_3Cl, -18.02; CH_2Cl_2, -19.86; $CHCl_3$, -22.19; CCl_4, -25.10. Combining these energies with the values of $\Delta(F^0-E_0^0/T)$ we obtain the free energy of formation of these compounds (Table X). The vapor pressures of CH_2Cl_2, $CHCl_3$ and CCl_4 are 0.570, 0.264 and 0.150 atmos., respectively.[22] Thus one has,

$C_{\beta g}+H_2+Cl_2=CH_2Cl_2$ (1) $\Delta F_{298}^0=-15.25$ Kcal./mole,

$C_{\beta g}+\frac{1}{2}H_2+\frac{3}{2}Cl_2=CHCl_3$ (1) $\Delta F_{298}^0=-16.52$,

$C_{\beta g}+2Cl_2=CCl_4$ (1) $\Delta F_{298}^0=-17.23$.

Bichowsky and Rossini[19, 20] from the various measurements on the equilibrium, $Cl_2+CO=Cl_2CO$, estimate ΔH_{291}^0 to be -53.5 Kcal./mole. This corresponds to $\Delta E_0^0=-52.7$. Using this figure for ΔE_0^0 we have calculated the free energy of formation of phosgene.

Table X contains the free energy of formation of the chloromethanes, formaldehyde and phosgene at one atmosphere.

Following other workers[28, 29] in this field we have used the *International Critical Tables* values for the fundamental physical constants.

TABLE X.

T°K	H_2CO	CH_2Cl_2	$CHCl_3$	CCl_4	CH_3Cl	$COCl_2$
298.1	−26.5	−14.9	−15.7	−16.1	−13.6	−50.3
350	−26.2	−13.8	−14.4	−14.5	−12.5	−49.8
400	−25.9	−12.1	−13.1	−12.9	−11.4	−49.2
500	−25.2	−10.2	−10.5	− 9.9	− 9.0	−48.2
600	−24.4	− 7.8	− 7.9	− 6.7	− 6.6	−47.1
700	−23.6	− 5.4	− 5.2		− 4.0	−46.1
800	−22.8	− 2.9	− 2.3		− 1.5	−45.0
900	−21.9				+ 1.2	−43.8
1000	−21.0				3.8	
1100	−20.1				6.5	
1200	−19.2				9.1	
1300	−18.3					
1400	−17.4					
1500	−16.5					

ΔF° of formation of the gases at 1 atmos.

[27] Johnston and Walker, J. Am. Chem. Soc. **55**, 172 (1933).

[28] Giauque, J. Am. Chem. Soc. **52**, 4808 (1930).

[29] Cross, J. Chem. Phys. **3**, 167 (1935).

Propagation of Sound in Gases

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The propagation of sound and supersonic waves in gases has been attacked by Kneser, Richards and Reid, Rose, and others, without taking viscosity and heat conduction into account. Bourgin neglects viscosity. Herzfeld and Rice have taken heat conduction and viscosity into account along with the effect of internal temperature lag of one state. In the present paper, these effects are considered together with the effect of many internal energy states. The general equation is derived for wave propagation in a pure gas of any number of energy states. The probability constants involved are functions of temperature and gas composition only. This equation is first solved for the case of a single two state gas. The solution is then extended to mixtures of gases, including air.

I. Velocity and Absorption in a Pure Gas With any Number of Energy States

A

WHEN a sound or supersonic wave is propagated through a gas, a compression is accompanied by a rise in temperature and an increase in pressure. The respective changes, δT, δp, and $\delta\rho$ in temperature, pressure and density, as well as the mass velocity, u, have phase relations which depend upon the undisturbed conditions of the gas and the frequency of the wave. If the gas contains molecules in various states (e.g., those having energy of translation only, others having vibrational or rotational energy as well), the number of molecules per unit volume in the ith state, N_i, will depend upon the total number of molecules N, upon the temperature, T, and also upon the phase relations between δN_i, δN, and δT. This last dependency is most easily described from the physical conditions which effect the change in N_i, namely, the number of collisions between particles in different energy states and the probability that a particular class of collisions will result in a particular type of transition from one energy state to another.

$$\frac{\partial N_i}{\partial t}=\frac{\partial N_i}{\partial N}\frac{\partial N}{\partial t}+\sum_j N_j\sum_k[N_k(f_{ki})_j-N_i(f_{ik})_j]. \tag{1.01}$$

The first term on the right of (1.01) is the rate of change of N_i because of the compression of the gas; the second is the additional rate of change of N_i because of collisions and is dependent on temperature changes. The number of collisions per second of a certain type (as between molecules in the jth and kth state) is proportional to the product N_jN_k. The number of transitions per second of a given type is proportional to the number of these collisions per second and thus proportional to N_jN_k. The proportionality constant $(f_{ki})_j$[1] relates the product N_jN_k to the number of transitions from the kth state to the ith state per second, and so on. In each case the internal subscripts designate the transition under consideration, and the external subscript designates the state of the molecule with which the transition molecule collides. Now

$$N_i=N_{i0}+\delta N_i \tag{1.02}$$

and

$$(f_{ki})_j=(f_{ki})_j{}^0+\delta(f_{ki})_j. \tag{1.03}$$

Also the principle of detailed balancing may be stated:

$$[N_{k0}(f_{ki})_j{}^0-N_{i0}(f_{ik})_j{}^0]=0. \tag{1.04}$$

We have, upon substituting (1.02), (1.03), and (1.04) in (1.01):

$$\frac{\partial(\delta N_i)}{\partial t}=\frac{\partial(\delta N_i)}{\partial(\delta N)}\frac{\partial(\delta N)}{\partial t}+\sum_j N_{j0}\sum_k[\delta N_k(f_{ki})_j{}^0-\delta N_i(f_{ik})_j{}^0]+\sum_j N_{j0}\sum_k[N_{k0}\delta(f_{ki})_j-N_{i0}\delta(f_{ik})_j]. \tag{1.05}$$

[1] With this treatment $(f_{ki})_j$ and $(S_{ki})_j$ to be introduced later, are dependent only upon gas composition and temperature. This simple dependence is not possible for parameters relating transition rates to a fixed number of molecules under consideration. In this connection as well as in some others, our method of attack is very similar to that of D. G. Bourgin, Phys. Rev. **42**, 721 (1932).

Assuming that for given colliding states, k and j, $(f_{ki})_j$ depends only on the kinetic energy of the colliding molecules, i.e., on the temperature, and is always in equilibrium with the temperature, $\delta(f_{ki})_j$ may be calculated from equilibrium conditions. We have for the last expression in brackets in (1.05)

$$N_{k0}\delta(f_{ki})_j - N_{i0}\delta(f_{ik})_j = \left[N_{k0}\frac{\partial(f_{ki})_j}{\partial T} - N_{i0}\frac{\partial(f_{ik})_j}{\partial T}\right]\delta T. \quad (1.06)$$

Furthermore, since the principle of detailed balancing is fulfilled at all temperatures, (1.04) gives

$$0 = \frac{\partial}{\partial T}[N_{k0}(f_{ki})_j^0 - N_{i0}(f_{ik})_j^0]$$

$$= \frac{\partial N_{k0}}{\partial T}(f_{ki})_j^0 - \frac{\partial N_{i0}}{\partial T}(f_{ik})_j^0 + N_{k0}\frac{\partial(f_{ki})_j^0}{\partial T} - N_{i0}\frac{\partial(f_{ik})_j^0}{\partial T}.$$

Using (1.04) again and the equation

$$\frac{\partial N_{k0}}{\partial T} = \frac{N_{k0}\epsilon_k}{kT^2},$$

in which k is Boltzmann's constant, and ϵ_k is the energy associated with the kth state of one molecule, we find

$$N_{k0}\frac{\partial(f_{ki})_j^0}{\partial T} - N_{i0}\frac{\partial(f_{ik})_j^0}{\partial T} = \frac{(f_{ki})_j^0 N_{k0}(\epsilon_i - \epsilon_k)}{kT^2}. \quad (1.07)$$

Substituting (1.07) in (1.06) gives us the evaluation we desire.

It will be observed that N_r and $(f_{rs})_t$ occur in (1.05) only with zero subscripts or superscripts, indicating equilibrium values, constants for given undisturbed conditions. Accordingly, the zero subscripts and superscripts will henceforth be omitted though understood. (1.05) now becomes

$$\frac{\partial(\delta N_i)}{\partial t} = \frac{\partial(\delta N_i)}{\partial(\delta N)}\frac{\partial(\delta N)}{\partial t} + \sum_j N_j \sum_k \left[(f_{ki})_j \delta N_k - (f_{ik})_j \delta N_i + \frac{(f_{ki})_j N_k(\epsilon_i - \epsilon_k)\delta T}{kT^2}\right]. \quad (1.08)$$

When we observe that

$$[\partial(\delta N_i)]/[\partial(\delta N)] = N_i/N$$

and assume that all changes are of the form $Ae^{j\omega t}$, (1.08) goes over into

$$j\omega\delta N_i = \frac{j\omega N_i \delta N}{N} + \sum_j N_j \sum_k \left[(f_{ki})_j \delta N_k - (f_{ik})_j \delta N_i + \frac{(f_{ki})_j N_k(\epsilon_i - \epsilon_k)\delta T}{kT^2}\right]. \quad (1.09)$$

We now introduce the following simplifying notation:

$$\rho_0 S_{ki} = \sum_j N_j (f_{ki})_j, \qquad \rho_0 Q_i = \sum_j \sum_k N_j (f_{ik})_j = \rho_0 \sum_k S_{ik}, \quad (1.10)$$

and obtain on substituting in (1.09) and again using (1.04)

$$(\rho_0 Q_i + j\omega)\delta N_i = \frac{j\omega N_i}{N}\delta N + \rho_0 \sum_k S_{ki}\delta N_k + \rho_0 \sum_k N_k(\epsilon_i - \epsilon_k) S_{ki}\delta T/kT^2. \quad (1.11)$$

From Eqs. (1.11), for the various values of i, δN_i may be solved for in terms of δN and δT.

B

The equation of continuity, and the equation of motion (written to include the effect of viscosity) yield for the complex velocity of sound, v', (defined by $u = u_0 e^{j\omega(t - x/v')}$)

$$v'^2 = \delta p/\delta\rho + j4\eta\omega/3\rho. \quad (1.12)$$

It should be noted that this complex velocity includes absorption. (See Eq. (2.09).) Using the general gas law to eliminate δp we have

$$v'^2 = \frac{RT}{M}\left(1 + \frac{\rho}{T}\frac{\delta T}{\delta\rho}\right) + j4\eta\omega/3\rho. \quad (1.13)$$

The equation of energy may be written

$$ML\frac{\partial^2 T}{\partial x^2}=-RT\frac{\partial \rho}{\partial t}+C_\infty \rho\frac{\partial T}{\partial t}$$
$$+\sum_i \epsilon_i M\left(\frac{\partial N_i}{\partial t}-\frac{N_i}{N}\frac{\partial N}{\partial t}\right), \quad (1.14)\ ^{2}$$

in which C_∞ is the molar heat at constant volume associated with the external degrees of freedom, ϵ_i is the internal energy of a single molecule in the ith state, and L is the coefficient of heat conduction. The last term in (1.14) is necessary because (since the equation is written for a fixed number of molecules) the quantity $\partial N_i/\partial t$ must have subtracted from it that part of itself which is caused by compression.

When we assume $\delta\rho \thickapprox \delta T \thickapprox \delta N_i \thickapprox e^{j\omega(t-x/v')}$ Eq. (1.14) takes the form

$$(\rho C_\infty - j\omega ML/v'^2)\delta T - RT\delta\rho$$
$$=-\sum_i \epsilon_i M(\delta N_i - N_i \delta N/N). \quad (1.15)$$

The right-hand member may be evaluated from equations (1.11), the ϵ_i generally being known from spectroscopic data. Then $\delta T/\delta\rho$ in (1.13) can be determined and v'^2 becomes completely specified.

II. Two-State Gas

A

For the two-state gas, the subscript k in (1.11) takes on the values 0, and 1. Then $Q_0=S_{01}$ and $Q_1=S_{10}$. Eq. (1.11) therefore becomes:

$$(\rho_0 S_{10}+j\omega)\delta N_1=\frac{j\omega N_1}{N}\delta N+\rho_0 S_{01}\delta N_0$$
$$+\frac{\rho_0 N_0}{kT^2}\epsilon_1 S_{01}\delta T, \quad (2.01)$$

and taking into account

$$\delta N=\delta N_1+\delta N_0, \quad (2.02)$$

we get

$$[\rho_0(S_{10}+S_{01})+j\omega]\delta N_1$$
$$=\left(\rho_0 S_{01}+\frac{j\omega N_1}{N}\right)\delta N+\frac{\rho_0 N_0}{kT^2}\epsilon_1 S_{01}\delta T. \quad (2.03)$$

Rose[3] has demonstrated that certain types of collisions produce a higher order effect and may be neglected. If this is done, S_{10} and S_{01} have a different interpertation but otherwise equation (2.03) is unchanged.

An alternative way of writing (2.03) which will be more useful in subsequent development is

$$[\rho_0(S_{01}+S_{10})+j\omega]\delta N_1=\left(\rho_0 S_{01}+\frac{j\omega\rho_1}{\rho}\right)\frac{R\delta\rho}{Mk}$$
$$+\frac{R\rho_0^2}{Mk^2T^2}\epsilon_1 S_{01}\delta T, \quad (2.04)$$

in which k is Boltzmann's constant.

If we now use the value of δN_1, given in (2.04), in Eq. (1.15) and solve for $\delta T/\delta\rho$, there results:

$$\frac{\delta T}{\delta\rho}=\frac{RT(S_{10}+j\omega/\rho)}{(\rho C_\infty - j\omega ML/v'^2)(S_{10}+j\omega/\rho)+R\rho_1\rho_0\epsilon_1^2 S_{10}/\rho k^2T^2}. \quad (2.05)$$

In obtaining the last equation we made use of the fact that $S_{01}=N_1 S_{10}/N_0$ for a two-state gas, and consequently $[(\rho_1/\rho)(S_{01}+S_{10})-S_{01}]=0$.

[2] In the Landau-Teller theory (Physik. Zeits. Sowjetunion, July 1936), $\sum_i \epsilon_i\left(\frac{\partial N_i}{\partial t}-\frac{N_i}{N}\frac{\partial N}{\partial t}\right)$ is replaced by $\epsilon\frac{dZ}{dt}$ where Z is the total number of vibrational quanta associated with the fixed number of molecules, N, under consideration. They proceed to show that for the case of a single vibrational mode, which is harmonic with evenly spaced energy levels, $dZ/dt=kN[k_{01}(Z+N)-k_{10}Z]$, in which K is the proportionality constant relating $N\bar{N}_i$ to number of collisions experienced by a molecule in the ith vibrational state per second, and k_{ij} is a second proportionality constant relating number of collisions per second experienced by molecules in the ith vibrational state to number of transitions per second from the ith to the jth state. In what follows in their paper, they treat k, k_{01}, and k_{10} as constants. This procedure, though frequently resorted to in papers on sound propagation, is unjustified. k depends upon both pressure and temperature, and k_{ij} on temperature. The importance of this paper should not be overlooked, however, since it appears that the authors have introduced a great simplification for cases in which higher vibrational levels are of importance. But in the many cases where the ratio N_{i+1}/N_i is small (about 0.0005 for O_2 at room temperature), the higher levels may be neglected with sufficient precision.

[3] M. E. Rose, J. Chem. Phys. 2, 260 (1934).

Eliminating $\delta T/\delta\rho$ from (2.05) and (1.13) gives

$$v'^2=\frac{RT}{M}\left[1+\frac{j4\eta\omega M}{3\rho RT}+\frac{R}{C_\infty}\frac{S_{10}+j\omega/\rho}{[S_{10}(1+R\rho_1\rho_0\epsilon_1^2/C_\infty\rho^2k^2T^2)+\omega^2ML/\rho^2v'^2C_\infty+j\omega(1-MLS_{10}/v'^2C_\infty)/\rho]}\right]. \tag{2.06}$$

At this point we can make the single simplifying assumption that MLS/v'^2C_∞ is negligible in comparison to 1. We also make use of the relation

$$\left(1+\frac{R\rho_1\rho_0\epsilon_1^2}{C_\infty\rho^2k^2T^2}\right)=C_0/C_\infty. \tag{2.07}$$

Then, separating v'^2 into its real and imaginary parts we obtain

$$v'^2=\frac{RT}{M}\left[1+\frac{R}{C_\infty}\frac{S_{10}^2C_0/C_\infty+\omega^2/\rho^2}{S_{10}^2C_0^2/C_\infty^2+\omega^2/\rho^2+M^2L^2\omega^4/v'^4C_\infty^2\rho^4}\right]$$
$$+\frac{j\omega}{\rho}\left[4\eta/3+\frac{R^2T}{MC_\infty}\frac{S_{10}(C_0-C_\infty)/C_\infty+(\omega^2ML/\rho^2v'^2C_\infty)}{S_{10}^2C_0^2/C_\infty^2+\omega^2/\rho^2+M^2L^2\omega^4/v'^4C_\infty^2\rho^4}\right]. \tag{2.08}$$

The complex velocity of sound, v', is related to the real velocity, v, and the absorption constant per wave-length, μ, as follows:

$$1/v'=(1-j\mu/4\pi)/v. \tag{2.09}$$

Inverting and squaring, and neglecting $\mu^2/16\pi^2$ in comparison with unity, we find

$$v'^2=v^2(1+j\mu/2\pi). \tag{2.10}$$

Comparing (2.10) and (2.08) there are obtained the equations for v^2 and μ:

$$v^2=\frac{RT}{M}\left[1+\frac{R}{C_\infty}\frac{S_{10}^2C_0/C_\infty+\omega^2/\rho^2}{S_{10}^2C_0^2/C_\infty^2+\omega^2/\rho^2+M^2L^2\omega^4/v^4C_\infty^2\rho^4}\right], \tag{2.11}$$

$$\mu=\frac{2\pi\omega}{\rho}\frac{\frac{4\eta M}{3RT}\left(\frac{S_{10}^2C_0^2}{C_\infty^2}+\frac{\omega^2}{\rho^2}+\frac{M^2L^2\omega^4}{v^4C_\infty^2\rho^4}\right)+\frac{R}{C_\infty}\left(\frac{C_0-C_\infty}{C_\infty}S_{10}+\frac{\omega^2ML}{\rho^2v^2C_\infty}\right)}{C_0(R+C_0)S_{10}^2/C_\infty^2+(R+C_\infty)\omega^2/C_\infty\rho^2+M^2L^2\omega^4/v^4C_\infty^2\rho^4} \tag{2.12}$$

One important special case occurs when, in (2.12), the terms involving η and L do not become appreciable until such high frequency is reached that the constant terms in this equation involving S_{10} are negligible in comparison with the terms in ω^2/ρ^2. In this case the fraction on the right side of (2.12) can be separated into two parts, and the equation written in the form

$$\mu=\frac{2\pi\omega}{\rho}\left[\frac{R(C_0-C_\infty)S_{10}}{(R+C_0)C_0S_{10}^2+(R+C_\infty)C_\infty\omega^2/\rho^2}\right.$$
$$\left.+\frac{C_\infty}{R+C_\infty}\left(\frac{4\eta M}{3RT}+\frac{MLR}{v^2C_\infty^2}\right)\right], \tag{2.13}$$

in which the first term is important at relatively lower and the second at relatively higher frequencies. In the lower frequency region μ goes through a maximum at some critical frequency, and, neglecting the second term, the value of μ_m is found to be

$$\mu_m=\frac{\pi R(C_0-C_\infty)}{(C_0C_\infty(R+C_0)(R+C_\infty))^{\frac{1}{2}}}. \tag{2.14}$$

Such cases are discussed, for instance, by Knudsen.[4] We believe our (2.13) and (2.14) to be more precise than the corresponding Knudsen-Kneser[5] formulas because of the simplifying assumptions they have made, but doubt if the difference can be detected experimentally.

[4] V. O. Knudsen, J. Acous. Soc. Am. **5**, 112 (1933).
[5] H. O. Kneser, Ann. d. Physik **11**, 761 (1931).

In this case, we may consider also the effect at very high frequencies when $\mu^2/16\pi^2$ is not negligible in comparison to unity. Then

$$v^2=(\text{real part } v'^2)(1+\mu^2/16\pi^2) \qquad (2.15)$$

to a sufficient approximation. Under these circumstances, using (2.13) and retaining the first-order terms only, we obtain

$$v^2=\frac{RT}{M}\left\{1+\frac{R}{C_\infty}\frac{S_{10}^2C_0/C_\infty+\omega^2/\rho^2}{S_{10}^2C_0^2/C_\infty^2+\omega^2/\rho^2}+\frac{\omega^2C_\infty}{\rho^2(R+C_\infty)}\right.$$
$$\left.\times\left(\frac{4\eta^2M^2}{9R^2T^2}+\frac{2L\eta M^2}{3v^2C_\infty^2T}-\frac{M^2L^2R(3R+4C_\infty)}{4v^4C_\infty^4}\right)\right\}. \qquad (2.16)$$

(2.13) and (2.16) should be especially useful over a wide range of values of ω/ρ. However, the approximations made should be criticially scrutinized in connection with any particular application.

A second special case, that of the one-state gas, is also important. The value of μ may be obtained directly from (2.13) by dropping out the first term

$$\mu=\frac{2\pi\omega C_\infty}{\rho(R+C_\infty)}\left(\frac{4\eta M}{3RT}+\frac{MLR}{v^2C_\infty^2}\right). \qquad (2.17)$$

Similarly, (2.16) becomes

$$v^2=\frac{RT}{M}\left\{1+\frac{R}{C_\infty}+\frac{\omega^2C_\infty}{\rho^2(R+C_\infty)}\left[\frac{4\eta^2M^2}{9R^2T^2}+\frac{2L\eta M^2}{3v^2C_\infty^2T}-\frac{M^2L^2R(3R+4C_\infty)}{4v^4C_\infty^4}\right]\right\}. \qquad (2.18)$$

In these last two equations C_∞ is identical with C_0. These equations must be equivalent to those obtained by Herzfeld and Rice[6] for a one-state gas since our fundamental equations become identical with theirs for this case.

Herzfeld[7] has carried out a more detailed analysis of the case of the one-state gas. He finds other effects on velocity of comparable magnitude to those of heat conduction and viscosity. The additional terms obtained for absorption are too small to be detected experimentally.

III. Mixture of Gases: Propagation in Air

This case is of particular importance because it includes air. In strict treatment for air, one would consider the carbon dioxide component as a three-state gas, since two vibrational modes in pure carbon dioxide are sufficiently excited to be of importance at room temperature. However, since one of these modes, the transverse vibration, is so much more important than the other and since the carbon dioxide content of air is small, this transverse vibration alone may be treated. Then, air is included under the case of a mixture of one-state and two-state gases.

It is necessary to include a new symbolism as follows:

$h_j=N_j/N$ the numerical fraction of the mixture composed of molecules of the jth component,

$M=\sum_{j=1}^{n}h_jM_j$, the effective molecular weight of the mixture,

$C_\infty=\sum_{j=1}^{n}h_jC_{\infty j}$, effective C_∞ for the mixture.

Since a numerical subscript on an N, ρ or h denotes a particular component, a superscript (0 or 1) is used to denote molecules in the ground or first vibrational state. Thus ρ_3' is the density of the excited molecules of the third component. ρ_3, with no superscript, is used to denote total density of the third component. No subscript or superscript is used when reference is had to properties of the whole mixture.

We shall define $(S_i^k)_r$ by the relation

$$\frac{\rho\rho_i^0}{\rho_i}(S_i^k)_r=\sum_j N_j[(f_{ki})_j]_r.$$

Where the r denotes the gas component under consideration and N_j^0 and N_j' should be taken separately in the summation. For the two-state gas mixture only $(S_0')_r$ and $(S_1^0)_r$ will occur, and since these are related; $(S_1^0)_r=(N_r'/N_r^0)(S_0')_r$;

[6] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).
[7] K. F. Herzfeld, Ann. d. Physik **23**, 465 (1935).

we need use only the former, writing it S_r. S_r is dependent upon the composition of the mixture as well as the temperature.

L and η are the effective values for the mixture.

Equation (1.12) for the complex velocity of sound remains unchanged for this case. In order to keep equation (1.13) as it was, the above definition of M is necessary. The equation is renumbered

$$v'^2=\frac{RT}{M}\left(1+\frac{\rho}{T}\frac{\delta T}{\delta\rho}\right)+j\frac{4\eta\omega}{3\rho}. \tag{3.01}$$

(1.15) becomes

$$(\rho C_\infty - j\omega ML/v'^2)\delta T-\left(RT+\sum_i \epsilon_i\frac{\rho_i' M}{\rho M_i}\frac{R}{K}\right)\delta\rho=-\sum_i \epsilon_i M N_i'. \tag{3.02}$$

Eqs. (1.11) become

$$\delta N_i'=\frac{\left[\frac{\rho_i' M}{M_i}S_i+j\frac{\omega\rho_i' M}{\rho M_i}\right]\delta N+\frac{\rho\rho_i'\rho_i^0 R}{\rho_i M_i}\frac{\epsilon_i}{K^2T^2}S_i\delta T}{\rho S_i+j\omega}. \tag{3.03}$$

Substituting (3.03) in (3.02) and solving for $\delta T/\delta\rho$, we obtain, using $C_i'=C_{0i}-C_{\infty i}$ as the vibrational molar heat of the ith component, and $a_i=(h_i' C_i S_i)/C_\infty$:

$$\frac{\delta T}{\delta\rho}=\frac{RT\left[\left(1+\sum_i\frac{a_i S_i}{S_i^2+\omega^2/\rho^2}\right)+\frac{j\omega}{\rho}\left(\frac{ML}{v'^2C_\infty}+\sum_i\frac{a_i}{S_i^2+\omega^2/\rho^2}\right)\right]}{\rho C_\infty\left[\left(1+\sum_i\frac{a_i S_i}{S_i^2+\omega^2/\rho^2}\right)^2+\frac{\omega^2}{\rho^2}\left(\frac{ML}{v'^2C_\infty}+\sum_i\frac{a_i}{S_i^2+\omega^2/\rho^2}\right)^2\right]}. \tag{3.04}$$

When (3.04) is substituted in (3.01), there is obtained for v'^2:

$$v'^2=v^2(1+j\mu/2\pi)=\frac{RT}{M}\left\{1+\frac{R}{C_\infty}\frac{1+\sum_i\frac{a_i S_i}{S_i^2+\omega^2/\rho^2}}{\left(1+\sum_i\frac{a_i S_i}{S_i^2+\omega^2/\rho^2}\right)^2+\frac{\omega^2}{\rho^2}\left(\frac{ML}{v'^2C_\infty}+\sum_i\frac{a_i}{S_i^2+\omega^2/\rho^2}\right)^2}\right.$$
$$\left.+\frac{j\omega}{\rho}\left[\frac{4\eta M}{3RT}+\frac{\frac{ML}{v'^2C_\infty}+\sum_i\frac{a_i}{S_i^2+\omega^2/\rho^2}}{\left(1+\sum_i\frac{a_i S_i}{S_i^2+\omega^2/\rho^2}\right)^2+\frac{\omega^2}{\rho^2}\left(\frac{ML}{v'^2C_\infty}+\sum_i\frac{a_i}{S_i^2+\omega^2/\rho^2}\right)^2}\right]\right\}. \tag{3.05}$$

It follows that

$$v^2=\frac{RT}{M}\left[1+\frac{R}{C_\infty}\frac{1+\sum_i\frac{a_i S_i}{S_i^2+\omega^2/\rho^2}}{\left(1+\sum_i\frac{a_i S_i}{S_i^2+\omega^2/\rho^2}\right)^2+\frac{\omega^2}{\rho^2}\left(\frac{ML}{v^2C_\infty}+\sum_i\frac{a_i}{S_i^2+\omega^2/\rho^2}\right)^2}\right], \tag{3.06}$$

$$\mu=\frac{2\pi\omega}{\rho}\left[\frac{4\eta M}{3RT}+\frac{\dfrac{ML}{v^2C_\infty}+\sum_i\dfrac{a_i}{S_i^2+\omega^2/\rho^2}-\dfrac{4\eta M}{3C_\infty T}\left(1+\sum_i\dfrac{a_iS_i}{S_i^2+\omega^2/\rho^2}\right)}{\left(1+\sum_i\dfrac{a_iS_i}{S_i^2+\omega^2/\rho^2}\right)^2+\dfrac{\omega^2}{\rho^2}\left(\dfrac{ML}{v^2C_\infty}+\sum_i\dfrac{a_i}{S_i^2+\omega^2/\rho^2}\right)^2+\dfrac{R}{C_\infty}\left(1+\sum_i\dfrac{a_iS_i}{S_i^2+\omega^2/\rho^2}\right)}\right]. \tag{3.07}$$

The square of a summation in the denominator is rather cumbersome. The operation may be carried out for the general case, however, yielding these forms:

$$v^2=\frac{RT}{M}\left[1+\frac{R}{C_\infty}\frac{1+\sum_i\dfrac{a_iS_j}{S_i^2+\omega^2/\rho^2}}{1+\dfrac{\omega^2M^2L^2}{\rho^2v^4C_\infty^2}+\sum_i\dfrac{a_i(a_i+2S_i+2\omega^2ML/\rho^2v^2C_\infty)}{S_i^2+\omega^2/\rho^2}+\sum_{i,j}\dfrac{2a_ia_j(S_iS_j+\omega^2/\rho^2)}{(S_i^2+\omega^2/\rho^2)(S_j^2+\omega^2/\rho^2)}}\right], \tag{3.06'}$$

$$\mu=\frac{2\pi\omega}{\rho}\left[\frac{4\eta M}{3RT}+\frac{\dfrac{ML}{v^2C_\infty}+\sum_i\dfrac{a_i}{S_i^2+\omega^2/\rho^2}-\dfrac{4\eta M}{3C_\infty T}\left(1+\sum_i\dfrac{a_iS_i}{S_i^2+\omega^2/\rho^2}\right)}{1+\dfrac{R}{C_\infty}+\dfrac{\omega^2M^2L^2}{\rho^2v^4C_\infty^2}+\sum_i\dfrac{a_i[a_i+(2+R/C_\infty)S_i+2\omega^2ML/\rho^2V^2C_\infty]}{S_i^2+\omega^2/\rho^2}+\sum_{i,j}\dfrac{2a_ia_j(S_iS_j+\omega^2/\rho^2)}{(S_i^2+\omega^2/\rho^2)(S_j^2+\omega^2/\rho^2)}}\right]. \tag{3.07'}$$

in which $\sum_{ij}$ means that each combination of i, j $(i\neq j)$ is to be taken once.

Various approximations may be made for special cases. If, for instance, there is but one two-state gas present in the mixture, or if all components but one may be treated as one-state gases in the range of ω/ρ under consideration, the last summation in the denominator is zero and the remaining summation signs may be dropped along with the subscript i. One then obtains, multiplying numerator and denominator by $S^2+\omega^2/\rho^2$, and neglecting $M^2L^2S^2/v^4C_\infty^2$ and $2MLa/v^2C_\infty$ in comparison to unity:

$$v^2=\frac{RT}{M}\left[1+\frac{R}{C_\infty}\frac{S(S+a)+\omega^2/\rho^2}{(S+a)^2+\omega^2/\rho^2+M^2L^2\omega^4/v^4C_\infty^2\rho^4}\right], \tag{3.08}$$

$$\mu=\frac{2\pi\omega}{\rho}\left[\frac{4\eta M}{3RT}+\frac{a+\dfrac{ML}{v^2C_\infty}(S^2+\omega^2/\rho^2)-\dfrac{4\eta M}{3C_\infty T}[S(S+a)+\omega^2/\rho^2]}{(S+a)\left(S+a+\dfrac{R}{C_\infty}S\right)+\dfrac{\omega^2}{\rho^2}(1+R/C_\infty)+\dfrac{\omega^4M^2L^2}{\rho^4v^4C_\infty^2}}\right]. \tag{3.09}$$

For the further specialization of making this single two-state gas, the only component present in the mixture, (3.08) and (3.09) reduce respectively to (2.11) and (2.12) affording a check on the work of this part of the paper.

When the effects of heat conduction and viscosity are negligible, a very considerable simplification of (3.06′) and (3.07′) results. The simplification is so obvious that we do not record it here.

The Kinetics of the Reaction $H+C_2H_6=CH_4+CH_3$

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The production of methane in the reaction between hydrogen atoms and ethane has been investigated by the discharge-tube method. It is found that the reaction $H+C_2H_6=CH_4+CH_3$ proceeds with an activation energy of 8.6 Kcal. (assuming a steric factor of 0.1) in satisfactory agreement with the value of 7.2 Kcal. found by Trenner, Morikawa, and Taylor. The error introduced by methane formation into Steacie and Phillips' determination of the activation energy of the reaction $D+C_2H_6=HD+C_2H_5$ appears to be negligible on the basis of the present results. At present no explanation can be offered of the discrepancy between the results of Trenner, Morikawa, and Taylor, and of Steacie and Phillips for the latter reaction.

INTRODUCTION

IN their classical investigation of the reactions of hydrogen atoms, Bonhoeffer and Harteck[1] found that luminescence occurs on mixing hydrogen atoms and ethane, but that the major part of the ethane is recovered unchanged at the end of the reaction. A further investigation was made by v. Wartenberg and Schultze[2] who found that there was a considerable loss of gas in their experiments (up to 25 percent), which might have been due to methane formed in the reaction, since with their technique methane would have passed through the liquid-air trap and been lost. They suggested that the main process was

$$C_2H_6+H=C_2H_5+H_2$$
$$C_2H_5+H+M=C_2H_6+M.$$

Chadwell and Titani,[3] in the course of another investigation, also made two experiments with ethane and hydrogen atoms. They found less than 5 percent of methane in the ethane after an experiment, i.e., less than 2.5 percent decomposition of ethane to form methane. They suggest that the gas lost in the investigation of v. Wartenberg and Schultze was ethane which passed the liquid-air trap, rather than methane. It is certainly to be expected that some ethane would be lost under the experimental conditions of v. Wartenberg and Schultze.

Steacie and Phillips[4] investigated the reaction of deuterium atoms with ethane. They assumed the primary step in the process to be

$$C_2H_6+D=C_2H_5+HD,$$

and found an activation energy of 6.3 Kcal. for the reaction. In their investigation they accepted the conclusion of Chadwell and Titani that methane formation was negligible, and determined the extent of the "exchange" by merely separating the hydrogen, burning the remaining products, and analyzing the resulting water for deuterium.

The reaction of deuterium atoms with ethane has recently been re-investigated by Trenner, Morikawa, and Taylor.[5] Their results differ sharply from those of Steacie and Phillips. At room temperature they conclude that the main reaction is

$$C_2H_6+D=CH_3D+CH_3 \quad (E=7.2 \text{ Kcal.}),$$

and that the exchange reaction is only appreciable at temperatures above 100°C, with an activation energy of 11.4 Kcal. In their experiments from 10 to 20 percent of the ethane was found to be decomposed to methane. They made very thorough analyses of the products of the reaction, and determined the deuterium content of each product separately. The methane formed was found to be about 50 percent deuterized, but the ethane was entirely light at temperatures below 100°C. They conclude that above 100°C the reaction also goes as suggested by Steacie and Phillips,

$$C_2H_6+D=C_2H_5+HD,$$

[1] Bonhoeffer and Harteck, Zeits. f. physik. Chemie **139**, 64 (1928).
[2] v. Wartenberg and Schultze, Zeits. f. physik. Chemie **B2**, 1 (1929).
[3] Chadwell and Titani, J. Am. Chem. Soc. **55**, 1363 (1933).
[4] Steacie and Phillips, J. Chem. Phys. **4**, 461 (1936).
[5] Trenner, Morikawa, and Taylor, J. Chem. Phys. **5**, 203 (1937).

but there is a very large discrepancy between the activation energies found in the two investigations (6.3 and 11.4 Kcal.).

Since Steacie and Phillips did not isolate the separate products, it follows that any deuteromethane formed in their investigation would be reported as deuteroethane. Their rates for the exchange reaction should therefore be too high on account of methane formation. The present investigation has been undertaken to determine the extent to which methane is formed under experimental conditions similar to those employed by Steacie and Phillips, and thus to determine the error, if any, introduced by this cause into their value of the activation energy of the exchange reaction.

Experimental

The general experimental arrangement was exactly the same as that employed in the previous investigation. Hydrogen was admitted to the system from cylinders at a constant rate and was pumped rapidly through the discharge and mixed with ethane. The ethane, methane, etc. were removed from the flowing stream and later analyzed.

The discharge was run on alternating current at about 3000 volts, the current through the tube being maintained constant at 350 milliamperes. Hydrogen passed through the discharge at a streaming velocity of about 1 liter per second and a pressure of about 0.3 mm, and entered a 1-liter reaction vessel. In this vessel it was mixed with ethane, and after a contact time of about 1 second, the mixture passed out of the reaction vessel. The walls of the system were poisoned in the usual way with phosphoric acid to cut down the rate of recombination of the hydrogen atoms.

The pumping system consisted of a three-stage diffusion pump backed by an oil pump. The speed at the entrance to the pump was about 20 liters per second.

The atom concentration in the reaction vessel was measured with a Wrede diffusion gauge of the usual type. At 20°C the mean value of the atom concentration was 24.1 percent, and at 200°C 18.6 percent.

As in the previous investigation, hydrocarbons were separated from hydrogen by adsorption on silica gel at −180°C in a trap situated between the diffusion pump and the backing pump. Check runs showed that hydrogen could be almost entirely separated from methane and ethane in this way, with very little loss of the hydrocarbons. The efficiency of the separation is illustrated by the data of Table I. In experiments in which higher hydrogen/ethane ratios were used correspondingly more hydrogen was recovered with the hydrocarbons, but the loss of hydrocarbons was not increased. The gases separated in this way were then analyzed by low temperature fractional distillation in a still of the Podbielniak type. In the distillation methane

Table I. *Efficiency of separation and recovery of gases.*

Entering Gas, cc			Desorbed Gas, cc			Hydrocarbon Lost, Percent
H_2	C_2H_6	CH_4	H_2	C_2H_6	CH_4	
1024	470	0	7	465	0	1.1
763	350	0	5	342	0	2.3
828	0	380	6	0	362	4.7
796	0	365	6	0	349	4.4

Table II. *Operating conditions.*

Discharge current = 350 ma
Volume of reaction vessel = 1370 cc

Run Nos.	Flow Rates cc/sec. at N. T. P.		Pressure, mm
	H_2	C_2H_6	
3, 4, 5	0.284	0.130	0.39
6, 7, 9, 10, 11	0.284	0.047	0.32
8	0.414	0.047	0.38

Table III. *The products of the reaction.*

Run No.	Gas Recovered, Percent				Decomposition, Percent	Remarks
	C_2H_6	CH_4	H_2	Higher products		
1	97.9	0.6	1.5	—	(0.2)	Blank experiment, no discharge
2	97.9	0.5	1.6	—	(0.2)	Blank experiment, no discharge
3	86.4	10.1	3.5	0.0	5.5	
4	83.7	12.8	3.5	0.0	7.1	
5	82.6	13.3	4.1	0.0	7.4	
6	75.0	18.0	7.0	0.0	10.7	
7	76.3	17.6	6.1	—	10.3	
8	70.2	22.8	7.0	—	13.8	
9	70.5	21.0	8.5	—	12.9	Walls of system very wet
10	54.2	38.2	7.6	0.0	26.0	200°C
11	59.2	35.5	5.3	0.0	23.1	200°C

TABLE IV. *The rate of reaction.*

RUN NO.	TEMP., °C	COLLISION YIELD	E, KCAL., ASSUMING A STERIC FACTOR OF 0.1	
3	20	2.5×10^{-8}	8.9	
4	20	3.3×10^{-8}	8.8	
5	20	3.4×10^{-8}	8.8	Mean value at 20°C =8.6
6	20	4.9×10^{-8}	8.5	
7	20	4.7×10^{-8}	8.5	
8	20	5.9×10^{-8}	8.4	
9	20	5.9×10^{-8}	8.4	
10	200	3.1×10^{-7}	12.0	
11	200	2.8×10^{-7}	12.1	

and hydrogen were taken off together, and this fraction was analyzed by combustion.

The ethane used was taken directly from cylinders supplied by the Ohio Chemical and Manufacturing Co. It was stated by them to contain better than 97.0 percent ethane. Analyses by low temperature distillation, and for olefins by the usual absorption method, showed the following impurities:

CH_4+H_2 less than 0.3 percent
C_2H_4 1.3 percent
higher hydrocarbons less than 0.3 percent.

No olefins were present in the products of an experiment, showing that the initial 1.3 percent of ethylene must have largely disappeared, presumably by hydrogenation, during the process.

The operating conditions are summarized in Table II. In general an experiment lasted for from 90 to 180 minutes, and was continued until some 600–700 cc of ethane had been put through the system. This gave a sample large enough to analyze accurately by the distillation method.

RESULTS

The analyses of the products of the reaction are given in Table III. It is evident that a considerable amount of ethane is decomposed to methane, in agreement with the findings of Trenner, Morikawa, and Taylor.

Calculation from the above data gives the values of the collision yield and of the activation energy given in Table IV. It will be seen that the mean value of the activation energy of the reaction

$$H+C_2H_6=CH_4+CH_3$$

is 8.6 Kcal. when the calculations are made from collision yields at room temperature. This is in good agreement with the value calculated in the same way by Trenner, Morikawa, and Taylor. A considerably higher activation energy is obtained from the collision yield at 200°C. In other words, the temperature coefficient of the reaction is much lower than would be anticipated from the collision yield at room temperature. This is also in agreement with the results of Trenner, Morikawa, and Taylor, who found practically no change in the methane yield with increasing temperature. It seems probable that this effect is to be associated with a diminution in the hydrogen atom concentration in the presence of ethane at higher temperatures, where the reactions

$$C_2H_6+H=C_2H_5+H_2$$
$$C_2H_5+H=C_2H_6$$

are becoming more prominent.

TABLE V.

	VALUES GIVEN BY STEACIE AND PHILLIPS	CORRECTED VALUES
Mean D content of ethane, percent	15.8	11.3
Mean "percent exchange"	25.4	18.7
Mean collision yield	1.86×10^{-6}	1.37×10^{-6}
E, Kcal., assuming a steric factor of 0.1	6.3	6.4

DISCUSSION

It is evident from the above results that the conclusions of Trenner, Morikawa and Taylor regarding the formation of methane in the reaction of hydrogen atoms with ethane have been completely confirmed. It remains to discuss the effect of this production of methane on the calculated value of the activation energy of the exchange reaction previously given by Steacie and Phillips.

In Steacie and Phillips investigation of the exchange reaction the mean D content of "ethane" from runs at room temperature was 15.8 percent. The present work shows, however, that this "ethane" was really $C_2H_6+CH_4$. The mean value of the amount of decomposition of ethane from the present work is 8.2 percent. Trenner, Morikawa and Taylor's investigation indicates that this methane is about 53.5 percent

exchanged. It follows that in Steacie and Phillips' work the apparent D content of ethane due to the presence of deuteromethane was 5.7 percent. Allowing for this we obtain the corrections to Steacie and Phillips' data shown in Table V.

It follows that the formation of methane found here introduces only a negligible correction into Steacie and Phillips' value of the activation energy of the exchange reaction.

The formation of methane is not, therefore, a sufficient explanation of the discrepancy between the results of Steacie and Phillips and of Trenner, Morikawa, and Taylor for the exchange reaction. In order to explain this discrepancy on the basis of methane formation in Steacie and Phillips' investigation, it would be necessary to assume that 60 percent of their ethane decomposed, as compared with a mean value of 8.2 percent found here. It does not appear to be possible at the moment to offer any explanation of the lack of agreement between the two investigations.

It was pointed out in the previous paper that the activation energy of the reaction

$$H+C_2H_6=C_2H_5+H_2$$

is of considerable importance in connection with the Rice-Herzfeld free radical chain theory.[6] It was shown that an activation energy of 6.3 Kcal. for this reaction introduces insurmountable difficulties into the application of the scheme to the ethane decomposition. It is worth pointing out that even the much higher value of Trenner, Morikawa, and Taylor would introduce serious difficulties into the application of the scheme. Also, the presence of the reaction

$$H+C_2H_6=CH_4+CH_3$$

with an activation energy of about 8 Kcal. would fundamentally alter the nature of the chain carrying steps in the Rice-Herzfeld scheme, and would destroy its agreement with experiment.

[6] Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

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The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K to the Boiling Point. The Heat of Vaporization and Vapor Pressure. The Equilibria $N_2O_4=2NO_2=2NO+O_2$

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The heat capacity of nitrogen tetroxide has been measured from 15°K to the boiling point, 294.25°K. The melting point is 261.90°K. The heats of fusion and vaporization were found to be 3502 and 9110 cal./mole, respectively. The vapor pressures of solid and liquid nitrogen tetroxide were measured with a mercury manometer by means of an arrangement in which carbon dioxide protected the mercury surface from reaction with the nitrogen tetroxide. The data have been represented by the equations: Liquid nitrogen tetroxide 261.90 to 294.9°K $\log_{10} P$(int. cm Hg) $= -1753.000/T + 8.00436 - 11.8078 \times 10^{-4}T + 2.0954 \times 10^{-6}T^2$. Solid nitrogen tetroxide 240.3 to 261.90°K, $\log_{10} P$(int. cm Hg) $= -2460.000/T + 9.58149 + 7.6170 \times 10^{-3}T - 1.51335 \times 10^{-5}T^2$. By applying the third law of thermodynamics to the calorimetric measurements, the entropy of the gas, which is dissociated to the extent of 16.1 percent into nitrogen dioxide at the boiling point, was found to be 80.62 cal./deg. per mole of gas as N_2O_4. From a consideration of the available data on the equilibria $N_2O_4=2NO_2=2NO+O_2$ in combination with spectroscopic data for the several substances, and the experimental entropy value given above, a number of quantities of thermodynamic interest have been evaluated. For $N_2O_4(g)$, $S^0_{298.1}=72.73$ and for $NO_2(g)$, $S^0_{298.1}=57.47$ cal./deg. per mole. These values, which are the ones which should be used in ordinary thermodynamic calculations, do not include the nuclear spin entropy, $R \ln 3 = 2.183$, for each nitrogen atom. The absolute entropies are $N_2O_4(g)$, $S^0_{298.1}=77.10$; $NO_2(g)$, $S^0_{298.1}=59.65$ cal./deg. per mole. For the reactions: $2NO_2=N_2O_4$, $\Delta F^0_{298.1}=-1{,}110$ cal., $\Delta H^0_{298.1}=-13{,}693$ cal.; $N_2+2O_2=N_2O_4$, $\Delta F^0_{298.1}=23{,}440$ cal., $\Delta H^0_{298.1}=2{,}239$ cal.; $NO+\frac{1}{2}O_2=NO_2$, $\Delta F^0_{298.1}=-8{,}375$ cal., $\Delta H^0_{298.1}=-13{,}562$ cal.; $\frac{1}{2}N_2+O_2=NO_2$, $\Delta F^0_{298.1}=12{,}275$ cal., $\Delta H^0_{298.1}=7{,}964$ cal. The experimental entropy value obtained in this investigation, together with band spectrum data, has made possible a much better correlation of the various measurements on the above equilibria than has hitherto been possible. The good agree-

ment demonstrates that the entropy value obtained from the experimental measurements and the third law of thermodynamics is the correct one. In the course of the calculations several points concerning the molecular structures of nitrogen dioxide and nitrogen tetroxide were investigated. Accepting the band spectrum evidence, that NO_2 is a symmetrical nonlinear molecule, it was possible to show from the equilibrium measurements that the statistical weight of the normal electronic state is 2. One would also infer this from existing magnetic data which are consistent with the value to be expected from a $^2\Sigma$ state. It is difficult to draw accurate conclusions with respect to the structure of the N_2O_4 molecule; however, the experimental entropy value seems to be more consistent with the symmetrical form O_2N-NO_2 which would have considerably less entropy than would be expected in the case of an unsymmetrical N_2O_4 molecule. The measurements exclude the possibility of free rotation of NO_2 groups in symmetrical O_2N-NO_2. The calculations do not permit an estimate of the potential barrier concerned in the rotational oscillations of these groups. An extensive summary of the $N_2O_4=2NO_2=2NO+O_2$ equilibria data is given.

THE determination of the entropies of nitrogen tetroxide and nitrogen dioxide gases from the third law of thermodynamics is complicated by the fact that these two substances are present at appreciable mole fractions under all conditions of equilibrium between the liquid and gaseous states. Although the dissociation equilibrium has been repeatedly studied during the past fifty years it has not been found possible to obtain the entropy change of the reaction $N_2O_4=2NO_2$ from the equilibrium measurements alone without an uncertainty of several entropy units per mole. It is desirable to obtain the entropies of gases to about a tenth of an entropy unit.

In order to obtain accuracy the following procedure was adopted: The entropy of the gas in equilibrium with liquid at the boiling point was evaluated in the usual way from the third law of thermodynamics. Then

$$S^0_{\text{mixture}}=(1-\alpha)S^0_{N_2O_4}+2\alpha S^0_{NO_2}$$

$$-(1-\alpha)R\ln\frac{1-\alpha}{1+\alpha}-2\alpha R\ln\frac{2\alpha}{1+\alpha} \quad (1)$$

where α is the degree of dissociation of N_2O_4. The equilibrium concentrations of the two gases are known with sufficient accuracy and the entropy of nitrogen tetroxide can be found if an independent value of the entropy of nitrogen dioxide is obtained. Unfortunately the spectroscopic interpretation of the nitrogen dioxide molecule is not sufficiently complete to permit the full use of this method. The molecule is known to be triangular in shape and electron diffraction measurements have indicated the approximate values of its moments of inertia. The three fundamental vibration frequencies are known from its band spectrum. Nitrogen dioxide contains an odd number of electrons so there must be a multiplicity due to the unbalanced electron moment. Fortunately the equilibrium $2NO_2=2NO+O_2$ has been carefully investigated and the spectroscopic interpretations of nitric oxide and of oxygen are exceptionally well known. Thus it is possible, by methods which will be discussed later, to make an evaluation of the entropy of nitrogen dioxide from these data. The *a priori* weight of the normal electronic state was taken as $p_e=2$, in agreement with experiments by Havens,[1] who found that the magnetic susceptibility of nitrogen dioxide corresponded to the spin of one electron. Having obtained a reliable value for the entropy of nitrogen tetroxide by the above procedure, it has been possible to give a very satisfactory treatment of the equilibrium data for the reaction $N_2O_4=2NO_2$.

The calorimetric apparatus and procedure have been described previously.[2]

TABLE I. *Melting point of nitrogen tetroxide.*

TIME	% MELTED	T, °K RESISTANCE THERMOMETER	T, °K THERMOCOUPLE
8:55 A.M.		Heated into melting point	
12:07 P.M.	20	261.86	261.84
12:53 P.M.		Supplied heat	
2:23 P.M.	40	261.88	261.87
3:48 P.M.	40	261.88	261.87
4:30 P.M.		Supplied heat	
6:55 P.M.	60	261.89	261.89
7:41 P.M.		Supplied heat	
9:52 P.M.	80	261.89	261.90
10:16 P.M.	80	261.89	261.90
		Accepted value	261.90

[1] Havens, Phys. Rev. **41**, 337 (1932).
[2] Kemp and Giauque, J. Am. Chem. Soc. **59**, 79 (1937).

TABLE II. *Vapor pressure of nitrogen tetroxide. Boiling point 294.25°K (0°C=273.10°K).*

T, °K		P	$P_{obs.}-P_{calc.}$		$T_{obs.}-T_{calc.}$	
THERMOCOUPLE	RESISTANCE THERMOMETER	INTERNATIONAL CM (Hg)	THERMOCOUPLE	RESISTANCE THERMOMETER	THERMOCOUPLE	RESISTANCE THERMOMETER
240.298	240.296	1.997	−0.001	−0.001	+0.007	+0.005
240.315	240.322	2.011	+ .009	+ .008	− .046	− .040
248.476	248.476	4.358	− .002	− .002	+ .004	+ .004
255.622	255.620	8.246	+ .002	+ .004	− .003	− .006
258.782	258.782	10.821	+ .026	+ .029	− .029	− .032
261.875	261.884	13.975		Triple point with 40% melted.		
261.890	261.904	13.973		Triple point with 70% melted.		
(261.90)	(261.90)	(13.978)		Triple point, accepted values.		
264.042	264.050	15.825	− .008	− .015	+ .009	+ .016
268.043	268.041	19.872	− .007	− .005	+ .007	+ .005
271.943	271.940	24.666	+ .005	+ .009	− .003	− .006
275.939	275.929	30.563	− .002	+ .014	+ .001	− .009
279.326	279.324	36.493	+ .001	+ .005	− .000	− .003
284.217	284.212	46.785	− .010	+ .002	+ .004	− .001
288.202	288.210	56.945	− .014	− .037	+ .007	+ .013
292.137	292.138	68.807	+ .002	− .002	− .000	+ .000
294.898	294.893	78.329	− .004	+ .014	+ .001	− .004

NITROGEN TETROXIDE

Preparation

C.P. lead nitrate was dried in an oven for twelve hours at 120°C. The lead nitrate was then placed in a reaction flask attached to the preparation line and a vacuum of 10^{-5} mm Hg was obtained throughout the preparation system. The reaction flask was heated to 200°C by means of an electric oven and pumped until there was no sign of water condensing in the cold part of the line. The oven temperature was then raised to about 450°C. The nitrogen tetroxide which was generated was passed through phosphorus pentoxide and finally condensed in a bulb cooled by a bath of solid carbon dioxide and ether. The oxygen which was produced with the nitrogen tetroxide was allowed to escape through a mercury bubbler trap. The first 10 cc of liquid condensed was discarded. Any oxygen entrapped in the solid nitrogen tetroxide was removed by subliming the nitrogen tetroxide and pumping on it with a high vacuum pump. By means of observations on the change of melting point with the percentage melted, and later, on the premelting heat capacities, the impurity was estimated to be about one part in ten thousand.

Melting point

The melting point was observed for various percentages of nitrogen tetroxide melted. Table I gives a summary of these observations.

The vapor pressure of nitrogen tetroxide

To permit the use of a mercury manometer for measuring vapor pressures of nitrogen tetroxide the gas pressure was balanced by an equal pressure of carbon dioxide. The liquid or solid nitrogen tetroxide was kept in the calorimeter during the measurements and the inlet line of the calorimeter was connected by means of capillary tubing to a manometer system filled with carbon dioxide. A stopcock was located in the middle of the capillary line and bulbs of about 25 cc capacity were located on each side of the stopcock. Also in order to determine, approximately, the carbon dioxide pressure needed, an auxiliary manometer could be connected to the calorimeter. In this manometer the nitrogen tetroxide was allowed to come in contact with the mercury. The resulting reaction corroded the mercury but the position of balance could be determined within about 0.5 mm Hg. The procedure for measuring vapor pressures was as follows: The calorimeter line was thoroughly swept out before each measurement by evaporating some of the material in the calorimeter. All other lines were completely evacuated at the same time. The calorimeter was then heated to the desired temperature. The approximate pressure was measured and the auxiliary line disconnected. The manometer system was then filled with carbon dioxide to approximately the correct pressure and the stop-

cock between the carbon dioxide and nitrogen tetroxide was opened. The two gases intermixed slightly in one of the mixing bulbs as the pressures equalized, but the capillary lines contained practically pure gases and eliminated any appreciable diffusion.

A Société Génevoise cathetometer with a precision of 0.002 cm was used to compare the mercury levels with a standard meter. A diagram of the manometer has been given previously.[3] The meniscus height corrections were taken from the work of Cawood and Patterson.[4] The standard acceleration of gravity was taken as 980.665 cm/sec.^{2} and the acceleration of gravity for this location was taken as 979.973 g/cm^2.[5] Other data needed to correct the pressures to international cm Hg were taken from the "I.C.T." A small correction, amounting to 0.25 mm Hg when the pressure was 1 atmosphere, was applied to the measurements to take account of the difference in density of the carbon dioxide and nitrogen tetroxide gases in the manometer system.

The data have been represented by the equations: Liquid nitrogen tetroxide 261.90 to 294.9°K,

$$\log_{10} P(\text{int. cm Hg}) = -1753.000/T + 8.00436 - 11.8078 \times 10^{-4}T + 2.0954 \times 10^{-6}T^2. \quad (2)$$

Solid nitrogen tetroxide 240.3 to 261.90°K,

$$\log_{10} P(\text{int. cm Hg}) = -2460.000/T + 9.58149 + 7.61700 \times 10^{-3}T - 1.51335 \times 10^{-5}T^2. \quad (3)$$

The observations have been compared with the equations in Table II. The temperatures were measured with both a thermocouple and a gold resistance thermometer. The vapor pressure measurements were made in a separate investigation about one year after the melting point observations, given in Table I, and the heat capacity measurements, which are to be presented below. The impurity, as estimated from the change of melting point with the fraction melted, was about 5 parts in 10,000 whereas the previous material contained only 1 part in 10,000 on a molal (N_2O_4) basis.

The vapor pressure of nitrogen tetroxide has been measured by Ramsay and Young,[6] Guye and Drouginine,[7] Scheffer and Treub,[8] Russ,[9] Baume and Robert,[10] and by Mittasch, Kuss and Schlueter.[11] The melting and boiling point observations of previous investigators are compared with the present results in Table III.

Measurement of the amount of nitrogen tetroxide

As nitrogen tetroxide boils at room temperature, it was possible to condense it in a weighed evacuated bulb and determine the amount in the calorimeter directly.

TABLE III. *Melting and boiling point temperatures of nitrogen tetroxide.*

Melting Point °K	Boiling Point °K	Observer
....	299	Gay Lussac[12] (1816)
....	301	Dulong[13] (1816)
259.6	....	Fritzsche[14] (1841)
....	295	Peligot[15] (1841)
261.6	....	Muller[16] (1862)
263	....	Deville and Troost[17] (1867)
....	294.74	Tharp[18] (1880)
....	295.6 at 750 mm	Nadejdine[19] (1885)
....	295.0	Bousfield[20] (1888)
262.96	....	Ramsay[21] (1890)
....	295.07	Tharp and Rodger[22] (1894)
262.15	299	Geuther, Bruni and Berti[23] (1900)
....	293 at 720 mm	Lunge and Berl[24] (1906)
263.5	295	Guye and Drouginine[7] (1910)
262.3	294.3	Scheffer and Treub[8] (1912)
262.7	....	Edgerton[25] (1914)
264.06	295–296	Oddo[26] (1915)
....	294.0	Mittasch, Kuss and Schlueter[11] (1926)
261.90	294.25	This research

[3] Giauque and Egan, J. Chem. Phys. **5**, 45 (1937).
[4] Cawood and Patterson, Trans. Faraday Soc. **29**, 1522 (1933).
[5] Sternewarte, Landolt, Börnstein and Roth, *Physikalische-chemische Tabellen* (Verlag Julius Springer, Berlin, 1923).
[6] Ramsay and Young, Phil. Trans. London **A177**, 71 (1887).
[7] Guye and Drouginine, J. Chim. Phys. **8**, 473 (1910).
[8] Scheffer and Treub, Zeits. f. physik Chemie **81**, 308 (1912).
[9] Russ, Zeits. f. physik Chemie **82**, 217 (1913).
[10] Baume and Robert, Comptes rendus **168**, 1201 (1919).
[11] Mittasch, Kuss and Schlueter, Zeits. f. anorg. allgem. Chemie **159**, 1 (1926).
[12] Gay Lussac, Ann. Chim. Phys. **1**, 394 (1816).
[13] Dulong, Ann. Chim. Phys. **2**, 317 (1816).
[14] Fritzsche, J. prakt. Chem. **22**, 21 (1841).
[15] Peligot, Ann. Chim. Phys. **2**, 58 (1841).
[16] Muller, Liebig's Ann. **122**, 1 (1862).
[17] Deville and Troost, Compt. rendus **64**, 237 (1867).
[18] Tharp, J. Chem. Soc. **37**, 244 (1880).
[19] Nadejdine, Bull. Acad. St. Petersburg **30**, 327 (1885).
[20] Bousfield, J. Chem. Soc. **53**, 621 (1888).
[21] Ramsay, Zeits. f. physik. Chemie **5**, 221 (1890).
[22] Tharp and Rodger, Phil. Trans. **185A**, 397 (1900).
[23] Geuther, Bruni and Berti, Gazz. Chim. Ital. **30**, ii, 151 (1900).
[24] Lunge and Berl, Zeits. f. angew. Chemie **19**, 807 (1906).
[25] Edgerton, J. Chem. Soc. **105**, 647 (1914).
[26] Oddo, Gazz. Chem. Ital. **45**. i. 433 (1915).

TABLE IV. *Heat capacity of nitrogen tetroxide, 0°C =273.10°K (molecular weight, 92.016; 1.9259 moles in calorimeter).*

T, °K	ΔT	C_p cal./deg./mole	T, °K	ΔT	C_p cal./deg./mole
16.80	2.765	1.315	148.89	4.859	18.26
19.10	1.979	1.833	153.87	5.098	18.65
21.46	2.829	2.370	158.93	4.908	19.01
24.11	2.626	3.000	163.83	4.739	19.35
26.95	3.041	3.718	168.69	4.789	19.66
30.18	3.389	4.539	173.79	5.037	20.03
33.70	3.680	5.442	178.90	4.861	20.39
38.51	5.672	6.544	184.06	5.089	20.72
44.08	5.351	7.652	189.40	5.105	21.12
49.10	4.585	8.546	194.62	4.929	21.53
54.09	4.388	9.345	199.98	5.335	21.93
58.84	5.036	10.02	205.60	5.138	22.32
62.23	5.309	10.52	210.97	4.961	22.73
63.66	4.528	10.76	216.37	4.792	23.10
67.31	4.814	11.16	221.53	4.635	23.50
72.44	5.416	11.68	226.30	5.087	23.83
77.66	5.015	12.32	232.37	5.360	24.31
82.52	4.707	12.77	238.12	5.172	24.78
87.50	5.231	13.35	243.65	5.011	25.19
93.03	5.844	13.88	249.27	5.259	25.60
98.69	5.460	14.41	254.65	4.320	25.94
103.99	5.147	14.87	258.26	1.921	26.23
109.02	4.885	15.26	261.90	Melting point	
113.77	4.549	15.66	265.44	3.146	32.79
118.69	5.217	15.99	269.91	4.492	32.92
123.82	4.967	16.40	275.38	5.212	33.10
128.86	5.041	16.82	281.19	5.033	33.34
133.97	5.192	17.19	286.86	4.955	33.60
140.15	4.998	17.58	291.28	2.739	33.74
144.09	4.797	17.95	294.25	Boiling point	

TABLE V. *Heat capacity of nitrogen tetroxide (molecular weight, 92.016). Values taken from smooth curve through observations.*

T, °K	C_p cal./deg./mole	T, °K	C_p cal./deg./mole
20	2.03	160	19.07
30	4.50	170	19.76
40	6.86	180	20.46
50	8.70	190	21.18
60	10.20	200	21.92
70	11.46	210	22.66
80	12.56	220	23.41
90	13.58	230	24.15
100	14.51	240	24.89
110	15.34	250	25.63
120	16.15	260	26.36
130	16.90	270	32.93
140	17.63	280	33.28
150	18.36	290	33.71

The heat capacity of nitrogen tetroxide

Table IV gives the observed heat capacities of nitrogen tetroxide. Table V contains the heat capacity values taken from the smooth curve. The data are shown in Fig. 1.

Heat of fusion

The heat of fusion was measured in the usual manner. Table VI summarizes the data.

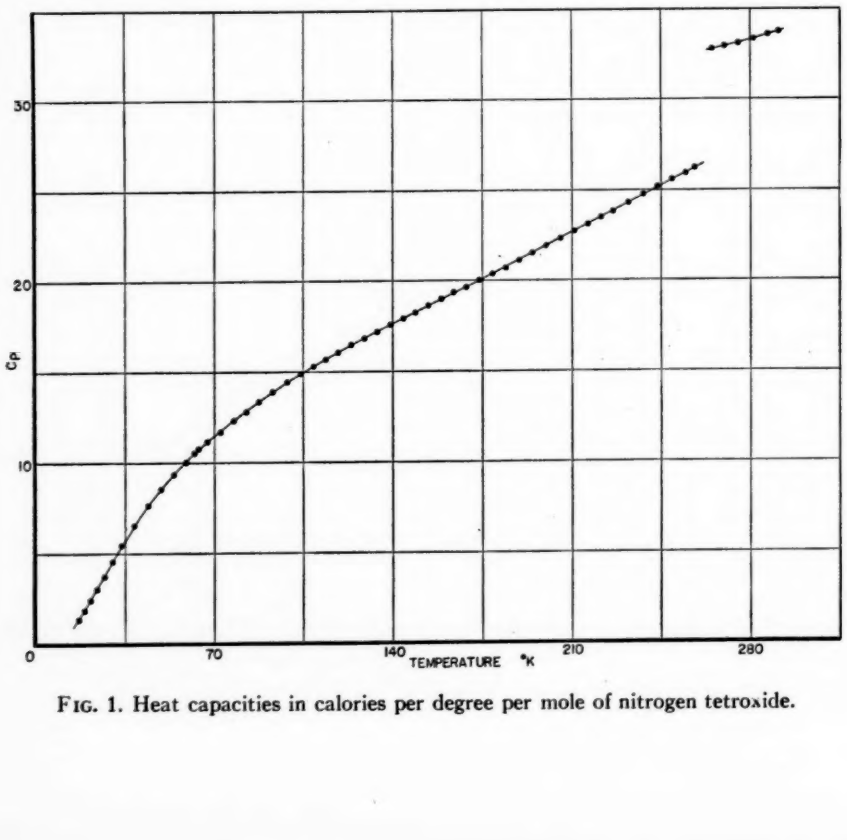


FIG. 1. Heat capacities in calories per degree per mole of nitrogen tetroxide.

Heat of vaporization

The nitrogen tetroxide vaporized during the heat of vaporization measurements was absorbed in alkali and the amount determined by the increase in weight of the absorption bulb. The gas was bubbled through a small mercury trap in the bottom of the absorption bulb. Each absorption bulb was filled with 150 cc of solution containing 63 grams of KOH and 25 grams of KI. Previous experiments had shown that the absorption bulb would become clogged with mercury salts in the absence of the KI. The results are summarized in Table VII.

A calculation of the heat of vaporization was made from the vapor pressure data, as represented by Eq. (2), by means of the equation

$$\Delta H = T\Delta V(dp/dT).$$

The calculation is complicated by uncertainties in the degree of dissociation and the correction for gas imperfection in the N_2O_4, NO_2 mixture. From the latter part of this paper α, the degree of dissociation was taken as 0.161, $(PV)_{N_2O_4} = RT(1-0.01P)$ and $(PV)_{NO_2} = RT(1-0.005P)$. The resulting value obtained for the heat of vaporization is 9233 cal./mole (92.016 g), as compared to the reliable calorimetric value 9110 cal./mole. The difference is within the limit of error of the gas imperfection correction.

The entropy from calorimetric data

Table VIII gives an itemized account of the entropy calculation for the equilibrium mixture of nitrogen dioxide and nitrogen tetroxide at the boiling point.

The free energy of nitrogen dioxide

Before interpreting the experimental result on the entropy of the gaseous mixture of nitrogen tetroxide and nitrogen dioxide it is necessary to obtain an independent value for the entropy of one of these gases. This is possible in the case of nitrogen dioxide. Spectroscopic observations on the vibrational frequencies of this molecule have been made by several experimenters. The data have been summarized by Sutherland and Penney[27] who give the values $\nu_1 = 641$, $\nu_2 = 1373$ and $\nu_3 = 1615$ cm^{-1}.

The moments of inertia have not been obtained spectroscopically but their product can be obtained by combining the molecular constants, which are known, with existing equilibrium data on the reaction, $NO_2 = NO + \frac{1}{2}O_2$. The above data are used with the equations

$$\Delta F^0/T = -R \ln K = \Delta(F^0 - H_0^0)/T + \Delta H_0^0/T \quad (4)$$

and for an asymmetrical top molecule

$$(F^0 - H_0^0)/T = -3/2R \ln M - 4R \ln T - R/2 \ln I_1 I_2 I_3 - R \ln p_e + R \ln \sigma - 257.401 + \sum_{\nu_1\nu_2\nu_3} F_{\text{vib}}/T \quad (5)$$

where I_1, I_2, I_3 are the principal moments of inertia, p_e is the *a priori* weight of the electronic state, σ is the symmetry number, which is equal to 2 in this case, and the other symbols have their usual meanings. $p_e = 2$ from the magnetic susceptibility determinations of Havens[1]

TABLE VI. *Heat of fusion of nitrogen tetroxide. Melting point 261.90°K, 0°C=273.10°K (molecular weight, 92.016).*

TEMPERATURE INTERVAL	CORRECTED HEAT INPUT/MOLE	$\int C_p dT$ +PREMELTING	ΔH CAL./MOLE
260.737–265.643	3676	176	3500
261.074–263.905	3584	85	3499
257.039–263.665	3748	242	3506
		Mean value	3502±3 cal.

TABLE VII. *Heat of vaporization of nitrogen tetroxide. Boiling point, 294.25°K; 0°C=273.10°K. Molecular weight, 92.016.*

MOLES VAPORIZED	TIME OF ENERGY INPUT, MINUTES	ΔH AT 760 MM CAL./MOLE
0.23860	70	9102
0.22359	65	9106
0.20846	65	9118
0.20949	65	9115
		Mean value 9110±9 cal.

TABLE VIII. *Calculation of the entropy of the equilibrium mixture.*

Debye function, 0–15°K	0.34
Graphical, 15–261.90°K	31.98
Fusion, 3502/261.90	13.37
Graphical, 261.90–294.25°K	3.87
Vaporization, 9110/294.25	30.96
	80.52±0.15
Correction for gas imperfection	0.10
Entropy of 92.016 g of equilibrium mixture of N_2O_4 and NO_2 gases at the boiling point.	80.62 E.U.

[27] Sutherland and Penney, Nature **136**, 146 (1935).

TABLE IX. *Calculation of ΔH_0^0 for the reaction $NO_2 = NO + \frac{1}{2}O_2$ from the data of Bodenstein and Lindner.*

T, °K	$-\log_{10} K$	DEVIATION FROM AV. ΔH_0^0
499.0	2.108	− 1
503.5	2.039	−36
519.4	1.876	*
519.6	1.867	− 8
521.9	1.850	12
564.1	1.422	24
570.5	1.353	1
577.6	1.288	11
593.2	1.134	−45
617.0	0.961	35
617.9	.943	−11
626.5	.878	− 5
627.6	.876	14
662.1	.620	− 6
668.4	.581	5
671.5	.559	7
685.1	.464	−17
699.9	.371	−11
727.8	.209	− 4
731.2	.190	− 2
733.3	.179	16
752.8	.068	−12
786.9	−.107	−11
792.4	−.125	19
796.4	−.149	8
798.6	−.158	3
799.9	−.164	8
825.4	−.285	− 9

Average value of ΔH_0^0 12795±13.

* Value not included in average.

mentioned above. The values of $(F^0 - H_0^0)/T$ for

$$\Delta\left(\frac{F^0-H_0^0}{T}\right)=\left(\frac{F^0-H_0^0}{T}\right)_{NO}+\frac{1}{2}\left(\frac{F^0-H_0^0}{T}\right)_{O_2}-\left(\frac{F^0-H_0^0}{T}\right)_{NO_2}. \quad (6)$$

nitric oxide have been tabulated by Johnston and Chapman[28] and those for oxygen have been calculated by Johnston and Walker.[29] For both oxygen and nitric oxide the values are based on very accurate spectroscopic data and are thus subject to practically no error.

The dissociation of nitrogen dioxide has been measured by Richardson,[30] by Bodenstein and Katayama,[31] and by Bodenstein and Lindner.[32] Only the data of Bodenstein and Lindner were considered in our final calculations; however summaries of the other data have been presented for the sake of completeness.

The value of the product $I_1 I_2 I_3$ was found by trial so that the value of ΔH_0^0 remained constant. The results are given below for the case $I_1 I_2 I_3 = 1.44 \times 10^{-116}$ g³ cm⁶. In terms of entropy an error of 0.05 cal./deg. per mole would produce a linear trend of 16 calories in ΔH_0^0 over the range of temperature covered by the experiments. The values at the lower temperatures are somewhat more inaccurate because the degree of dissociation in this region was too small for the most accurate evaluation of the equilibrium constant.

The data of Bodenstein and Lindner[32] are presented in Table IX, those of Bodenstein and Katayama[31] in Table X. No corrections were made for the effect of gas imperfection of nitric

TABLE X. *Value of ΔH_0^0 for the reaction $NO_2 = NO + \frac{1}{2}O_2$ from the data of Bodenstein and Katayama.*

SERIES	TEMPERATURE RANGE, °K	NUMBER OF DETERMINATIONS	ΔH_0^0
I	521–890	8	12,534±383
II	517–849	8	12,330±195
III	506–976	16	12,717±217
IV	492–974	17	12,428±379
V	513–772	10	12,933±36
Total		59	12,593±253

TABLE XI. *Free energy of nitrogen dioxide and ΔF for $NO_2 = NO + \frac{1}{2}O_2$.*

T, °K	$-\left(\frac{F-H_0^0}{T}\right)_{NO_2}$	$-\Delta\left(\frac{F^0-H_0^0}{T}\right)$	$\Delta F^0_{cal.}$	$K=\frac{(NO)(O_2)^{\frac{1}{2}}}{(NO_2)}$
275	48.536	14.617	8775	1.060×10^{-7}
298.1	49.202	14.826	8375	7.229×10^{-7}
300	49.252	14.849	8340	8.385×10^{-7}
325	49.918	15.028	7911	4.781×10^{-6}
350	50.538	15.222	7467	2.172×10^{-5}
375	51.122	15.379	7028	8.008×10^{-5}
400	51.670	15.535	6581	2.534×10^{-4}
425	52.195	15.667	6137	6.978×10^{-4}
450	52.676	15.799	5886	1.384×10^{-3}
500	53.617	15.998	4796	8.006×10^{-3}
550	54 471	16.176	3898	2.824×10^{-2}
600	55.266	16.326	2999	8.082×10^{-2}
650	56.010	16.455	2099	1.968×10^{-1}
700	56.709	16.564	1200	4.220×10^{-1}
750	57.373	16.661	299	8.181×10^{-1}
800	57.992	16.753	− 607	1.469
850	58.583	16.833	−1513	2.455
900	59.152	16.901	−2416	3.870

[28] Johnston and Chapman, J. Am. Chem. Soc. **55**, 153 (1933).
[29] Johnston and Walker, J. Am. Chem. Soc. **55**, 172, 5075 (1933).
[30] Richardson, J. Chem. Soc. London **51**, 397 (1887).
[31] Bodenstein and Katayama, Zeits. f. physik. Chemie **69**, 26 (1909).
[32] Bodenstein and Lindner, Zeits. f. physik. Chemie **100**, 82 (1922).

oxide, oxygen or nitrogen dioxide in treating the dissociation of nitrogen dioxide as it may be shown from order of magnitude calculations, based on typical equations of state, that the effect is unimportant at the temperatures concerned.

The data of Richardson,[30] consisting of 14 determinations over the temperature range 495–767°K, lead to a value of $\Delta H_0^0 = 13{,}275 \pm 411$.

The molecular constants of nitrogen dioxide

It will be of interest at this point to draw certain conclusions about the molecular structure of the nitrogen dioxide molecule. The product

$$I_1 = 2M_O(d \sin\theta)^2,$$

$$I_2 = \frac{2M_O M_N}{2M_O + M_N}(d\cos\theta)^2,$$

$I_3 = I_1 + I_2$, where θ is the half-angle.

$$d = \left(\frac{I_1 I_2 I_3 (2M_O + M_N)^2}{8M_O^3 M_N \sin^2\theta \cdot \cos^2\theta [(2M_O + M_N)\sin^2\theta + M_N \cos^2\theta]} \right)^{1/6}. \quad (7)$$

$I_1 I_2 I_3 = 1.44 \times 10^{-116}$ g^3 cm^6 is probably known to about 5 percent and this value may be used to obtain a reliable equation relating angle and distance in the nitrogen dioxide molecule. The results of this calculation are presented in Table XII. Sutherland and Penney,[27] and Badger and Herzberg[27] have expressed the opinion that the band spectrum characteristics of nitrogen dioxide indicate an angle of 110–120°. The electron diffraction experiments of Maxwell, Mosley and Deming[33] showed that it was difficult to give an unambiguous interpretation of the electron diffraction results. Several alternative combinations of angle and distance were in agreement with their measurements. They considered the most reasonable possibilities to be N–O = 1.15A, $2\theta = 120°$; N–O = 1.15A, $2\theta = 90°$; and N–O = 1.30A, $2\theta = 90°$. If the angle lies between 90 and 120° an accurate value for the N–O distance can be given; however, in a personal communication, Professor Linus Pauling has expressed the opinion that the NO_2 angle may be greater than 120° by as much as 10 or 15°.

Another point of interest is that the agreement in Table IX is sufficient to determine the *a priori* weight of the normal electronic state as 2, independently of the magnetic susceptibility results of Havens,[1] mentioned above. The electron diffraction interpretation of Maxwell, Mosley and Deming[33] is sufficiently explicit to eliminate such possibilities as $p_e = 4$ and as a matter of fact our first calculations were made in this manner to establish the value of p_e.

[33] Maxwell, Mosley and Deming, J. Chem. Phys. **2**, 331 (1934).

Since the above calculations were made, a paper by Zeise,[34] treating the $NO_2 = NO + \frac{1}{2}O_2$ equilibrium in a somewhat similar manner, has appeared. He finds the *a priori* weight of the normal electronic state to be $p_e = 4$. We are not able to understand this result since essentially the same data are used. The present calculations have been carefully checked and it may be stated that the *a priori* weight of the normal state is unambiguously determined as 2 rather than 4, even without considering the magnetic data.

The entropy of nitrogen dioxide

With the above data it is possible to obtain a reliable value for the entropy of nitrogen dioxide.

$$S^0 = 3/2R \ln M + 4R \ln T + R/2 \ln I_1 I_2 I_3 - R \ln \sigma + R \ln p_e + 265.349 + \sum_{\nu_1\nu_2\nu_3} S_{\text{vib}}. \quad (8)$$

Substituting, in Eq. (8), the various values given above, the entropy of NO_2 at 25°C is found to

TABLE XII. *N–O distance in nitrogen dioxide as a function of the angle assumed* $I_1 I_2 I_3 = 1.44 \times 10^{-116}$ *g cm*^{2}.

2θ	$d \times 10^8$ cm
80	1.144 ± 0.01
90	1.120 ± 0.01
100	1.108 ± 0.01
110	1.111 ± 0.01
120	1.130 ± 0.01
130	1.165 ± 0.01
140	1.225 ± 0.01
150	1.324 ± 0.01

[34] Zeise, Zeits. f. Elektrochemie **42**, 785 (1936).

be 57.47 cal./deg. per mole. The above value, which is the one which should be used in ordinary thermodynamic calculations, does not include the nuclear spin entropy. For completeness the nuclear spin contribution, $R \ln 3 = 2.18$, is added to give the absolute entropy 59.65 cal./deg. per mole. The entropy of nitrogen dioxide at the boiling point of nitrogen tetroxide, 294.25°K is found to be 57.35 cal./deg. per mole.

The entropy of nitrogen tetroxide

Before applying Eq. (1), given above, the relative amounts of nitrogen dioxide and nitrogen tetroxide in the equilibrium mixture at the boiling point must be known.

The degree of dissociation of nitrogen tetroxide has been measured by Natanson and Natanson,[35] Bodenstein and Katayama,[31] Wourtzel,[36] Bodenstein and Boës,[37] and by Verhoek and Daniels.[38] Wourtzel, and Bodenstein and Boës carried out experiments both below and considerably above the boiling point. Verhoek and Daniels made isothermal measurements at many different pressures, at the three temperatures 25, 35 and 45°. Wourtzel's measurements were made at pressures of between 0.1 and 0.2 atmosphere, so that very little correction for gas imperfection is necessary. Bodenstein and Boës made six series of measurements with pressures which varied from 0.29 to 0.76 atmos. In order to obtain values at the boiling point the separate series were interpolated graphically. Values of $K_{294.25°}$ were then calculated for each series, using the formula $P_1V = P_0V_0(1+\lambda P)$ to correct for gas imperfection. P was taken as the total gas pressure. For NO_2, λ was assumed to be -0.005. This value corresponds to the λ calculated from Berthelot's equation for carbon dioxide. For N_2O_4, $\lambda = -0.01$. This approximate value was selected because it gave a reasonably constant series of dissociation constants from the data at various pressures, otherwise one might expect the value of λ to be somewhat larger numerically. Verhoek and Daniels corrected their data on the assumption that the gas mixture behaved like sulfur dioxide.

A preliminary calculation of ΔS for the reaction $N_2O_4 = 2NO_2$ showed the ΔS given by Verhoek and Daniels to be too high by about 2.8 cal./deg. per mole. This is principally due to the fact that the 20 degree range covered by their measurements is not sufficient to accurately determine the temperature coefficient. Accordingly the value for K(V. and D.) was obtained by extrapolating the value given at 298.1 to 294.25°K by means of the ΔS determined by this research. In a similar manner the value of K was calculated from the K given at 298.3° by Wourtzel. The resulting values for 294.25 are K(W.) = 0.106, K(V. and D.) = 0.105, and K(B. and B.) = 0.106 atmos. The value $K_{294.25} = 0.106$ was selected. The exactness of this choice, which corresponds to a degree of dissociation, $\alpha = 0.161$, does not greatly affect the final value for the entropy of nitrogen tetroxide; however this choice was found to be identical with the best value which could be selected after the final detailed calculations on all available data.

From Eq. (1)

$$S^0_{N_2O_4} = \frac{1}{1-\alpha} S_{\text{mixture (1 atmos.)}} - \frac{2\alpha S^0_{NO_2}}{1-\alpha} + R \ln \frac{1-\alpha}{1+\alpha} + \frac{2\alpha R}{1-\alpha} \ln \frac{2\alpha}{1+\alpha}. \quad (9)$$

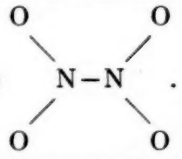
The values of the various quantities at the boiling point, 294.25°K, as given above, are $\alpha = 0.161$, $S^0_{\text{mixture}} = 80.62$ cal./deg. per mole, as N_2O_4, and $S^0_{NO_2} = 57.35$ cal./deg. per mole. The entropy of nitrogen tetroxide, N_2O_4, $S^0_{294.25}$ is 72.5 cal./deg. per mole. Then $N_2O_4 = 2NO_2$, $\Delta S^0_{294.25} = 42.2$ cal./deg.

This value of ΔS permits a more reliable correlation of the data at various temperatures than has previously been possible. The data could be treated by the more conventional thermodynamic methods; however, although the spectroscopic and other molecular data of nitrogen tetroxide are by no means complete, it appears advantageous to make use of such data as exist.

Sutherland[39] has offered an interpretation of

[35] Natanson and Natanson, Ann. d. Physik [3] **24**, 454 (1885); **27**, 606 (1886).
[36] Wourtzel, Comptes rendus **169**, 1397 (1919).
[37] Bodenstein and Boës, Zeits. f. physik. Chemie **100**, 75 (1922).
[38] Verhoek and Daniels, J. Am. Chem. Soc. **53**, 1250 (1931).
[39] Sutherland, Proc. Roy. Soc. London **A141**, 342 (1933).

the vibrational data obtained from the infrared absorption bands and Raman spectra. Sutherland suggests that the data are in best accord with the plane symmetrical structure



Hendricks[40] believes that x-ray data, obtained by Vegard,[41] indicate the symmetrical form given above, except that the NO_2 planes may be oriented at any angle between 0 and 25°. Pauling and Brockway[42] have suggested an unsymmetrical form, with a nitrogen oxygen linkage between the NO_2 groups, on the basis of the adjacent charge rule. The moments of inertia of nitrogen tetroxide have not been determined but order of magnitude calculations made in connection with present work, while perhaps not decisive, indicate that the symmetrical form is probably correct. The symmetrical forms would have a considerably smaller entropy and this seems more consistent with the experimental value determined from the third law of thermodynamics and dissociation equilibrium measurements.

The possibility of any considerable error in the third law value due to false equilibrium in the solid at low temperatures seems to be precluded by the agreement with equilibrium data over the range 282 to 404°K. The present entropy value definitely excludes free rotation of the NO_2 groups. The vibrational analysis is not sufficiently definite to permit an estimate of the potential barrier hindering the relative rotation of the NO_2 groups. The calculations to be given below assume that the barrier is high enough so that this motion can be treated as a harmonic oscillation.

The vibrational data relating to the twelve vibrational degrees of freedom of nitrogen tetroxide have been summarized by Sutherland.[39]

$\nu_1=1265$, $\nu_2=1360$, $\nu_3=752$, $\nu_4=813$, $\nu_5=1749$, $\nu_6=1724$, ν_7(torsion)$=?$, $\nu_8=283$, $\nu_9=380$, $\nu_{10}=500$, $\nu_{11}=(680)$, $\nu_{12}=(1480)$ cm^{-1}.

[40] Hendricks, Zeits. f. Physik **70**, 699 (1931).
[41] Vegard, Zeits. f. Physik **68**, 184 (1931).
[42] Pauling and Brockway, J. Am. Chem. Soc. **59**, 13 (1937).

The absorption spectrum of nitrogen tetroxide has been investigated and discussed by Harris and King,[43] who give the following frequency assignments: $\nu_1=1260$, $\nu_2=1360$, $\nu_3=752$, $\nu_4=813$, $\nu_5=\nu_6=1744$, ν_7(torsion)$=?$, $\nu_8=283$, $\nu_9=\nu_{11}=500\sim382$, $\nu_{10}=\nu_{12}=\sim682$ cm^{-1}. As pointed out by Harris and King,[43] three of the frequencies have a double weight when the NO_2 planes are perpendicular to each other.

For the purpose of the calculations given below the symmetrical perpendicular model was assumed. The following experimental values were used for the various frequencies: $\nu_1=1265$, $\nu_2=1360$, $\nu_3=752$, $\nu_4=813$, $\nu_5=\nu_6=1744$, ν_7(torsion)$=?$, $\nu_8=283$, $\nu_9=\nu_{11}=380$, $\nu_{10}=\nu_{12}=500$ cm^{-1}.

ν_7 was assumed to be low enough so that the equipartition value, R, of the heat capacity had been reached at room temperature. Except for the double frequencies no structural significance is attached to the various values and it may be shown that it is of little importance in the present calculations which two of the three values, 283, 380 and 500 cm^{-1}, are selected to have a double weight.

$$S^0_{N_2O_4}=3/2R\ln M+4R\ln T+R/2\ln I_1I_2I_3 - R\ln\sigma+265.349+\sum_{\nu_1\text{ to }\nu_{12}} S_{vib}. \quad (10)$$

From which

$$S^0_{N_2O_4}=5R\ln T+\sum_{\nu_1-\nu_6,\ \nu_8-\nu_{12}} S_{vib}+k_1. \quad (11)$$

$S^0_{N_2O_4}=72.5$ at 294.25°K and the constant, k_1, of Eq. (11) is 10.675 cal./deg. per mole.

TABLE XIII. *Free energy function of nitrogen tetroxide.*

T, °K	$-\left(\frac{F^0-H_0^0}{T}\right)_{N_2O_4}$	$-\Delta\left(\frac{F^0-H_0^0}{T}\right)_{N_2O_4=2NO_2}$
275	58.021	39.051
298.1	59.106	39.298
300	59.192	39.312
325	60.302	39.534
350	61.365	39.711
375	62.377	39.867
400	63.363	39.977
425	64.301	40.093

[43] Harris and King, J. Chem. Phys. **2**, 51 (1934).

TABLE XIV. *Calculation of ΔH_0^0 for the reaction $N_2O_4=2NO_2$ from the data of Bodenstein and Boës.*

T, °K	$\log_{10} K'$	α'	$\log_{10} K$	DEVIATION FROM AV. ΔH_0^0	T, °K	$\log_{10} K'$	α'	$\log_{10} K$	DEVIATION FROM AV. ΔH_0^0
281.82	−1.449	0.1593	−1.427	+ 3	338.69	0.351	0.6390	0.363	+ 2
282.58	−1.394	0.1934	−1.380	−21	339.53	0.379	0.5811	0.396	−15
284.56	−1.372	0.1473	−1.340	+10	341.02	0.407	0.6338	0.421	+ 6
285.04	−1.316	0.1823	−1.297	−10	342.57	0.459	0.7326	0.469	− 7
285.83	−1.273	0.2179	−1.261	−20	342.82	0.445	0.7734	0.452	+30
286.07	−1.323	0.1443	−1.285	+23	343.41	0.474	0.6473	0.489	− 5
287.89	−1.193	0.2354	−1.182	−24	344.19	0.493	0.6910	0.506	0
288.42	−1.185	0.2072	−1.168	−20	351.50	0.681	0.8025	0.693	−10
288.85	−1.197	0.1591	−1.161	− 7	352.56	0.696	0.8443	0.706	+10
289.56	−1.137	0.2483	−1.126	−19	353.21	0.709	0.7412	0.725	+ 5
291.17	−1.138	0.1757	−1.107	+31	353.91	0.732	0.7714	0.747	− 3
291.82	−1.091	0.1953	−1.067	+ 9	356.03	0.784	0.7559	0.802	−12
293.05	−1.022	0.2761	−1.012	− 6	356.60	0.798	0.7333	0.818	−16
294.20	−1.007	0.1773	−0.969	−10	361.96	0.903	0.8899	0.916	+26
295.09	−0.951	0.2599	−0.937	−12	362.41	0.949	0.8708	0.964	−36
297.44	−0.881	0.2174	−0.854	−16	363.26	0.932	0.8005	0.951	+17
302.07	−0.729	0.2763	−0.711	0	364.36	0.962	0.8183	0.981	+ 9
302.64	−0.749	0.3096	−0.737	+62	366.84	1.024	0.8524	1.044	− 4
306.24	−0.589	0.2655	−0.563	−16	369.12	1.079	0.8196	1.103	−19
305.84	−0.612	0.2887	−0.596	+12	372.12	1.139	0.8780	1.160	− 5
305.97	−0.587	0.4045	−0.580	− 5	372.98	1.146	0.9293	1.165	+17
313.48	−0.351	0.4873	−0.344	− 7	373.29	1.145	0.8566	1.169	+22
313.54	−0.347	0.4392	−0.338	−13	374.62	1.214	0.9189	1.234	−43
317.00	−0.291	0.3477	−0.270	+40	374.68	1.184	0.8727	1.209	+ 2
315.95	−0.284	0.4081	−0.271	− 4	383.19	1.352	0.8992	1.382	+ 8
316.47	−0.274	0.3883	−0.258	0	384.94	1.378	0.9092	1.410	+22
320.29	−0.159	0.4192	−0.143	− 3	385.34	1.444	0.9016	1.482	−91
323.96	−0.043	0.6019	−0.036	− 4	386.96	1.425	0.9270	1.459	+ 7
324.15	−0.036	0.5519	−0.027	− 9	387.49	1.412	0.9575	1.439	+59
326.00	0.014	0.4476	0.032	−19	390.84	1.543	0.9571	1.581	−77
326.24	0.015	0.5136	0.027	− 1	394.85	1.572	0.9367	1.612	+ 5
326.76	0.024	0.4912	0.038	+ 4	395.33	1.562	0.9312	1.600	+46
334.88	0.255	0.5655	0.270	− 9	398.22	1.660	0.9536	1.684	−10
334.87	0.254	0.7105	0.261	+ 4	403.93	1.744	0.9526	1.774	+17
335.51	0.276	0.6681	0.286	− 8					

Average value of ΔH_0^0, 12,873±16 cal.

The expression for the free energy of nitrogen tetroxide is

$$(F^0-H_0^0)/T=-\tfrac{3}{2}R\ln M-4R\ln T$$
$$-R/2\ln I_1I_2I_3+R\ln\sigma+4R$$
$$-265.349+\sum_{\nu_1 \text{ to } \nu_{12}}(F^0-H_0^0)_{\text{vib}}/T. \quad (12)$$

From which

$$(F^0-H_0^0)_{N_2O_4}/T=-5R\ln T$$
$$+\sum_{\nu_1-\nu_6,\ \nu_8-\nu_{12}}(F^0-H_0^0)_{\text{vib}}/T+5R-k_1. \quad (13)$$

The constants, k_1, of Eqs. (11) and (13) are identical.

The $(F^0-H_0^0)/T$ values for nitrogen tetroxide, as calculated from Eq. (13), are given in Table XIII. The values are given to 0.001 unit only for relative consistency.

In Table XIV the final calculations on the data of Bodenstein and Boës are given. In correcting for gas imperfection as a function of temperature the following considerations were used. As has been stated above the data over a considerable range of pressure at the boiling point, where gas imperfection is rather considerable, were found to be in agreement with the expression $P_1V=RT(1+\lambda P)$ where $\lambda_{N_2O_4}=-0.01$ and $\lambda_{NO_2}=-0.005$ atmos.$^{-1}$. It may be shown from Berthelot's equation of state that λ is approximately proportional to T^{-3}. Thus it was assumed that $\lambda_{N_2O_4}=-0.01(294/T)^3$ and $\lambda_{NO_2}=-0.005(294/T)^3$. The calculation of the equilibrium constant, K, in terms of fugacities is considerably simplified by the choice of $\lambda_{N_2O_4}=2\lambda_{NO_2}=\beta=-0.01(294/T)^3$.

$$K=\frac{4P(\alpha'+\beta P)^2}{1-(\alpha'+\beta P)^2}, \quad (14)$$

TABLE XV. *Calculation of ΔH_0^0 for the reaction $N_2O_4 = 2NO_2$ from the data of Wourtzel.*
Average value of ΔH_0^0, 12,876±14 cal.

T, °K	$\log_{10} K'$	$\log_{10} K$	DEVIATION FROM AV. ΔH_0^0
273.1	−1.756	−1.752	−16
273.1	−1.758	−1.754	−19
298.3	−0.835	−0.832	− 9
298.3	−0.841	−0.839	+ 1
298.3	−0.834	−0.832	− 8
323.4	−0.068	−0.064	+11
323.4	−0.073	−0.067	+16
323.4	−0.072	−0.062	+14
359.6	0.878	0.893	−27
359.6	0.855	0.870	+11
359.6	0.847	0.862	+24

where α' has been evaluated by neglecting gas imperfection.

$$\alpha' = \frac{(PV)_{obs}}{RT} - 1, \quad K' = \frac{4P\alpha'^2}{1-\alpha'^2}.$$

In Table XIV the second and third columns give α' and $\log_{10} K'$, the uncorrected values of Bodenstein and Boës. In column four the corrected $\log_{10} K$ is given. Column five gives the deviation from the average of values of ΔH_0^0 calculated from the relation

$$\Delta H_0^0/T = R \ln K + \Delta(F^0 - H_0^0)/T. \quad (15)$$

The average value, $\Delta H_0^0 = 12{,}873$ cal. per mole of N_2O_4, is in good agreement with the results over the entire range of temperature, 282 to 404°K. The deviations are somewhat larger at the extremes of the temperature region

TABLE XVI. *Calculation of ΔH_0^0 for the reaction $N_2O_4 = 2NO_2$ from the data of Verhoek and Daniels.*

P atmos.	$-\log_{10} K'$	$\log_{10} K$	DEVIATION FROM AV. ΔH_0^0
Temperature = 298.1°K			
0.1566	0.860	0.855	−18
0.2118	.848	.841	−37
.2172	.878	.871	+ 4
.5129	.859	.840	−38
.2889	.861	.851	−24
.6543	.878	.851	−24
.5699	.867	.845	−31
.3150	.893	.882	+19
.3271	.833	.822	−63
.3357	.870	.858	−14
.3660	.880	.867	− 2
.3793	.883	.870	+ 2
.3841	.880	.866	− 3
.3941	.873	.859	−12
.3942	.873	.859	−12
.4021	.880	.866	− 3
.4213	.885	.870	+ 2
.4369	.898	.883	+21
.4588	.888	.871	+ 4
.4598	.893	.876	+11
.4743	.860	.843	−34
.4843	.890	.872	+ 6
.5107	.856	.837	+57
.5254	.888	.868	0
.5435	.899	.878	+13
.5443	.895	.874	+ 8
.5554	.890	.869	+ 1
.5719	.889	.867	− 2
.5996	.850	.826	−56
.6007	.896	.872	+ 5
.6214	.914	.889	+29
.6349	.919	.893	+34
.6373	.950	.924	+77
.8081	.908	.871	+ 4
.8623	.893	.853	−21
Average value of ΔH_0^0, 12,907±20			

P atmos.	$-\log_{10} K'$	$-\log_{10} K$	DEVIATION FROM AV. ΔH_0^0
Temperature = 308.1°K			
0.2382	0·498	0.493	−38
.3533	.530	.522	+ 4
.3649	.510	.502	−23
.4086	.532	.523	+ 5
.4287	.530	.520	0
.4391	.530	.520	0
.4400	.522	.512	−11
.4871	.541	.529	+13
.5378	.544	.530	+14
.5659	.521	.507	−17
.5823	.544	.529	+13
.6623	.518	.500	−37
.7065	.578	.559	+65
.8902	.552	.525	+ 8
.9470	.554	.525	+ 8
Average value of ΔH_0^0, 12,878±17			
Temperature 318.1°K			
0.2662	0.169	0.164	−57
.4064	.188	.182	−29
.4554	.215	.209	+11
.4889	.214	.207	+ 8
.4903	.203	.196	− 8
.5446	.206	.198	− 5
.5985	.222	.213	+18
.6295	.201	.191	−15
.6484	.217	.207	+ 8
.7349	.200	.188	−19
.7834	.254	.240	+56
.9814	.243	.221	+28
1.0474	.227	.204	+ 4
Average value of ΔH_0^0, 12,862±20			

Average of the values for 25, 35 and 45°C = 12,882±19 cal.

covered by the experiments since either small or large values of the degree of dissociation make it difficult to accurately evaluate $K=4P\alpha^2/1-\alpha^2$. The greatest accuracy should be obtained in the region near $\alpha=0.7$.

The constancy of the ΔH_0^0 values in Table XIV shows that the value of the entropy of nitrogen tetroxide obtained from the third law of thermodynamics is correct. For example, if false equilibrium had existed in the solid at low temperatures during the heat capacity measurements, to an extent which produced an entropy error of $R \ln 2$, then the ΔH_0^0 values would have shown a trend of over 200 calories in Table XIV. Actually no significant drift is found.

The earlier data of Bodenstein and Katayama,[31] consisting of 20 determinations over the temperature range 291–367°K, lead to a value of $\Delta H_0^0=12{,}856\pm125$ cal. The deviations are considerably larger than those in the later work of Bodenstein and Boës so the above value was given no weight.

The data of Wourtzel have been considered in Table XV. The nitrogen tetroxide used in these measurements was obtained by mixing nitric oxide with excess oxygen. The total pressures, due to N_2O_4, NO_2 and O_2, were used in making the gas imperfection corrections. The corrections were quite small in this case since all of the experiments were carried out at rather low pressures. The average value of $\Delta H_0^0=12{,}876$ cal. per mole of N_2O_4 is in almost perfect agreement with that obtained from the measurements of Bodenstein and Boës.

The results obtained from the data of Verhoek and Daniels are shown in Table XVI.

While there is a small trend with temperature in the values of ΔH_0^0 shown in Table XVI, the average result, $\Delta H_0^0=12{,}882\pm19$ cal. per mole of nitrogen tetroxide, is in excellent agreement with the values, $12{,}873\pm16$, and $12{,}876\pm14$, calculated from the experiments of Bodenstein and Boës, and of Wourtzel, respectively.

The final value of ΔH_0^0 was taken as 12,875 cal. for the dissociation of 1 mole of N_2O_4. The first extensive experiments on the nitrogen tetroxide dissociation were carried out by Natanson and Natanson.[35] Their measurements were nearly all made under conditions where the degree of dissociation was near unity. These data have been calculated in detail leading to the result $\Delta H_0^0=13{,}500\pm600$ cal. As has been pointed out above, it is experimentally difficult to determine the dissociation constant accurately when α is near 1. Only 5 of their 49 measurements fall in the most favorable experimental region $\alpha^2=0.4$ to 0.6. The average, $\Delta H_0^0=12{,}901\pm33$ cal. for these five measurements, compares well with the more recent experiments.

TABLE XVII. *Data relating to the formation of nitrogen dioxide and nitrogen tetroxide.*

REACTION	ΔH_0^0 CAL.	$\Delta F^0_{298.1}$ CAL.	$\Delta H^0_{298.1}$ CAL.	$\Delta S^0_{298.1}$ CAL./DEG.
$2NO_2=N_2O_4$	−12875	−1110	−13693	−42.21
$N_2+2O_2=N_2O_4$	4333	23440	2239	−71.12
$NO+\frac{1}{2}O_2=NO_2$	−12771	−8375	−13562	−17.40
$\frac{1}{2}N_2+O_2=NO_2$	8602	12275	7964	−14.46

The various data make it possible to evaluate some quantities of especial interest for several reactions. Using the equations

$$\Delta F^0=T\Delta\left(\frac{F^0-H_0^0}{T}\right)+\Delta H_0^0 \qquad (16)$$

and

$$\Delta H^0=\Delta F^0+T\Delta S^0 \qquad (17)$$

together with the calculations of Giauque and Clayton[44] on the reaction

$$\tfrac{1}{2}N_2+\tfrac{1}{2}O_2=NO \qquad \Delta F^0_{298.1}=20{,}650 \text{ cal.}, \quad \Delta H_0^0=21{,}400 \text{ cal.},$$

the free energy and heat of reaction data tabulated in Table XVII are found. The entropies of NO,[28, 45] N_2,[44] and O_2[46] at 298.1°K were taken as 50.35, 45.79 and 49.03 cal./deg. per mole, respectively. The entropies of NO_2 and N_2O_4 calculated above are 57.47 and 72.73 cal./deg. per mole at 298.1°K, respectively.

[44] Giauque and Clayton, J. Am. Chem. Soc. **55**, 4875 (1933).
[45] Johnston and Giauque, J. Am. Chem. Soc. **51**, 3194 (1929).
[46] Giauque and Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).

LETTERS TO THE EDITOR

This section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($3.00 per page) will not be made and no reprints will be furnished free.

The Viscosity of Monolayers: Theory of the Surface Slit Viscosimeter

The surface viscosimeter which makes use of the flow of a film through a rectangular capillary slit possesses many advantages in comparison with other types. Perhaps the greatest of these is the fact that, since it has no moving parts, no motion is imparted to the substrate (usually aqueous) by the instrument. Since surface viscosimeters which utilize moving rings or disks impart such a motion, their theory is thus made much more complicated.

A surface slit viscosimeter has been used by Harkins and Myers [1] who also gave the first term on the right of Eq. (2) given below. Since this neglects the effects of the viscosity of the water carried along by the film, it is essential to develop the more complete theory, and this has been done by one of us (Kirkwood). This adds the last term in Eq. (2).

The hydrodynamical problem may be solved for an incompressible film of viscosity coefficient, η, and a fluid substrate of viscosity coefficient, η_0, flowing through a rectangular slit of width a and depth h. If α is the film pressure gradient $(f_2-f_1)/l$, the area flux, A is calculated to be

$$A=\frac{8\alpha a^3}{\pi^4}\sum_{n=1,\,3,\,5\cdots}^{\infty}\frac{1}{n^4[\eta+(a\eta_0/\pi n)\coth(\pi nh/a)]}. \quad (1)$$

If the ratio h/a of depth to breadth is large relative to unity, Eq. (1) leads to the following approximation, which is doubtless adequate for all practical purposes.

$$\eta=\alpha a^3/12A-a\eta_0/\pi. \quad (2)$$

The substrate correction to be applied to the earlier formula is thus equal to $a\eta_0/\pi$. In the above equations, no end corrections have been made, but they will be negligible if the ratio of the slit length, l, to the slit width, a, is made large.

On water at 20°C the corrections in surface poises are for different diameters of slit.

1 mm = 0.00032,
0.5 mm = 0.00016,
0.1 mm = 0.00003.

The correction terms to be applied to the values of Harkins and Myers are smaller than those given above, since they used a slit of negligible depth. Thus the value of 0.0018 surface poises, given as the viscosity of a film of arachidic acid, when corrected is close to 0.0017, a change within the experimental error. However, the values given earlier for extremely fluid films, such as that formed by oleic acid, should be considered as only upper limiting values. The exact values of the viscosities are now being determined.

A capillary slit was used by Bresler and Talmud [2] but they did not determine viscosities from rates of flow, and their theory is different from ours.

On account of the theoretical and practical merits of the surface slit viscosimeter, and its great simplicity of construction and use, it should be adopted as the standard for all surface viscosimetry.

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University of Chicago,
Chicago, Illinois,
November 16, 1937.

[1] W. D. Harkins and R. J. Myers, Nature **140**, 465 (1937). R. J. Myers and W. D. Harkins, J. Chem. Phys. **5**, 601–3 (1937).
[2] S. E. Bresler, B. A. Talmud, and D. L. Talmud, Physik. Zeits. Sowjetunion **4**, 864 (1933).